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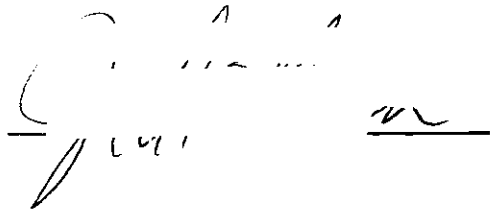

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THE PHOTOMETRIC TITRATION AND EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF NICKEL IN THE PRESENCE OF COBALT

A THESIS

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Joe Allen Mann

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THE PHOTOMETRIC TITRATION AND EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF NICKEL IN THE PRESENCE OF COBALT

Approved: _____

Chairman

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SUMMARY

In the present study, two methods for the determination of nickel in high purity cobalt have been developed. In both methods cobalt(II) is oxidized in ammoniacal medium by hydrogen peroxide, and the pentammine complex of cobalt(III) is formed. The formation of this complex renders cobalt unreactive toward EDTA and PAN. However, under the same conditions nickel reacts with both EDTA and PAN; thus, these two substances can be used for the determination of nickel.

Studies have also been made to demonstrate the effect of ionic strength on the degree of formation of the nickel-murexide complex.

Facile methods for reducing the nickel content of cobalt salts have also been developed and evaluated.

Photometric Titration of Traces of Nickel in Cobalt

Nickel can be determined via a photometric titration using EDTA as the titrant and murexide as the indicator. To the sample in solution, concentrated aqueous ammonia is added in excess of the amount necessary to convert cobalt(II) and nickel(II) to their soluble amine complexes. Hydrogen peroxide is added to the ammoniacal sample solution. The container of sample is placed in a water bath, kept at 70°C, for five minutes. A second portion of hydrogen peroxide is added, and the sample solution is heated for two additional minutes. The cobalt is converted to the pentammine complex of cobalt(III) and nickel remains as the hexammine complex of nickel(II). After the solution has cooled to room temperature,

it is diluted to approximately 120 ml, murexide is added, and an EDTA titration is performed at an operating wavelength of 442 nm. For the work here described, a semi-immersion phototitrator was used. Cobalt(III) pentammine does not react with either murexide or EDTA, while nickel forms a yellow murexide complex, which reacts quite readily with EDTA. Accurate and precise results have been obtained for Co:Ni ratios up to 10,000. A study of potentially troublesome metals has been made, and procedures have been developed to eliminate their interference. Thus, nickel can be determined in presence of all metals expected to be present in high purity cobalt.

Extractive Spectrophotometric Determination of Traces of Nickel in Cobalt

Nickel in high purity cobalt, can be determined spectrophotometrically as the red nickel-PAN chelate in the following manner. The sample is treated with aqueous ammonia and hydrogen peroxide and the pentammine complex of cobalt(III) and the hexammine complex of nickel(II) are formed. The sample solution is, then, carefully adjusted to pH 8.9 with 1:1 sulfuric acid. PAN is added and the solution is allowed to stand for 3.5 minutes. Nickel reacts with PAN but cobalt(III) pentammine does not. The nickel-PAN complex which forms and the excess PAN are extracted into chloroform, and the absorbance of the extract is measured at 568 nm. Accurate and precise results have been obtained for Co:Ni ratios up to about 200,000. A study of all potentially troublesome metals has been made and procedures have been developed to eliminate their interference.

Ionic Strength Effects on the Nickel-Murexide System

In the development of the above mentioned photometric titration of nickel using murexide as the indicator, it was found that the yellow nickel-murexide complex, which forms in ammoniacal solution, was destroyed when ammonium chloride was added for the purpose of establishing a buffer. Further investigations revealed that any salt, in even moderate concentration, would prevent the formation of the nickel-murexide complex. Furthermore, in solutions already containing the yellow complex, addition of salts would destroy the yellow color and produce the violet color of free murexide. All 1:1 electrolytes were found to exhibit the same behavior while 2:1 electrolytes had a greater effect. Sucrose was investigated, as an example of a nonelectrolyte, and was found to have essentially no effect on the formation of the nickel-murexide complex. It was thus, concluded that too high ionic strength in solution was responsible for the observed effect on the nickel-murexide system.

Facile Methods for Reducing the Nickel Content of Cobalt Salts

Two methods have been developed for the preparation of cobalt salts of very low nickel content.

In the first method, cobalt(III) hexammine trichloride is precipitated slowly according to the procedure of Bjerrum and McReynolds. Nickel does not precipitate under the conditions of the procedure. Two batches of cobalt salts containing 0.75% nickel (based on cobalt) were subjected to the procedure. The nickel content was reduced to 0.00076% and 0.005% in the two batches.

In the second method, cobalt salts are subjected to hydrogen per-

oxide in ammoniacal medium, with formation of the pentammine complex of cobalt(III). The pH of the resulting solution is reduced to a value of 8.9 with 1:1 sulfuric acid, PAN is added, and a chloroform extraction of the nickel panate and excess PAN is performed. The pentammine complex of cobalt(III) is then decomposed by heating with concentrated sulfuric acid. Cobalt(II) sulfate, thus prepared, was analyzed and no nickel could be detected.

CHAPTER I

INTRODUCTION

Historical

In the sixteenth century certain ores, which resembled copper ore, were discovered in the Harz Mountains of Germany. Attempts were made to extract copper from the ores, but all such attempts failed. Not only did the ores fail to yield copper, but in the roasting and smelting processes noxious fumes caused sickness and death among the people who mined and worked the ore. Because of its mysterious behavior the ore was given the name Kobald, the Germanic form of the Greek word meaning "devilish mountain spirit."

The residue from the roasted ore was fused with sand and potash to produce a blue glass. In 1742, G. Brandt showed that the blue color was caused by a new demi-metal which he named cobalt (1). Perhaps the name is somewhat undeserved, since the real "devilish mountain spirits," and hence the toxic properties of the ores, were due to compounds of arsenic. In 1780, Bergman studied the chemistry of cobalt and established it as a new element.

In 1751, nickel was discovered and recognized as a new element by A. F. Cronstedt at the Swedish Department of Mines (2,3). The mutual occurrence of nickel and cobalt in ores was soon recognized, and vain attempts to separate the two metals attested to their similar chemical behavior.

For several years following the discoveries of nickel and cobalt, little attention was given to their individual chemistry. However in the middle of the nineteenth century interest in uses of the metals began to increase. As interest in the metals mounted, new ores were discovered; and the development of methods for producing the individual metals from the ores became mandatory.

The methods for producing cobalt are numerous and varied as outlined by Young (1). Cobalt is recovered directly from its ores, and as a by-product from the refining of copper, nickel, iron and lead. The cobalt recovered by these processes generally is refined by either electrolytic reduction or selective reduction by hydrogen under high pressure. Even with several purification steps being carried out, cobalt and its salts are always contaminated by nickel. Therefore the determination of small amounts of nickel in cobalt and cobalt salts is of considerable importance.

The Current Problem of Determining Nickel in Cobalt

After repeated purification steps cobalt and its compounds usually contain from 10^{-1} to 10^{-4} weight-weight per cent nickel. The problem of determining nickel in presence of cobalt is not a simple one because of the chemical similarities of the two metals, and it is especially difficult if small amounts of nickel are to be determined. Although many methods have been developed for the determination of nickel, only a very few of them are applicable in presence of large amounts of cobalt. Most of these methods are limited to levels of no better than five per cent nickel in cobalt. These methods have been reviewed collectively by Dale

and Banks (4) and by Kodama (5). Some of the best methods for the determination of nickel in the presence of cobalt are discussed below. Most of these techniques require expensive instrumentation.

Spectrophotometric methods, which make use of the selectivity of dimethylglyoxime for nickel, were used for many years as standard methods for determining small amounts of nickel (6). A chloroform extract of the nickel-dimethylglyoximate is made, and the extract is subjected to a photometric measurement. The method is quite sensitive; however the sensitivity can be further increased by forming the nickel-dimethylglyoximate in presence of a strong oxidizing agent (7). A deep red solution forms which can be subjected to a spectrophotometric measurement.

However the reagent fails in the determination of trace amounts of nickel in presence of cobalt. The latter metal forms a complex with dimethylglyoxime and excessive amounts of the reagent are required to sufficiently satisfy the demand of cobalt and also to have some available for the nickel. In addition some of the cobalt complex is extracted and interferes with the nickel determination. The lower concentration limit for nickel in cobalt is, thus, restricted to about 0.05 per cent.

Polarography is difficult to use for determination of nickel in cobalt because of the close proximity of the waves of the two metals. However limited success can be achieved by employing complexing agents which serve to separate the two waves somewhat. Goto and Fukushi (8) have determined nickel polarographically in an ammoniacal medium at a level of 0.02 per cent in cobalt. Jackwerth and Höbel (9) have reported a cathode-ray polarographic determination of nickel in a pyridine and cyanide medium. Results were staisfactory at nickel levels as low as

0.003 per cent. However routine determinations were conveniently performed at only about 0.01 per cent.

Emission spectrography is very useful for the simultaneous determination of several elements of low concentrations in a matrix of either a known or nearly invarient composition. This technique can be used for determination of nickel in high purity cobalt. McClure and Kitson (10) used a direct current arc source with an open circuit of 240 volts and an arc current of ten amperes to determine nickel in a cobalt oxide matrix on a level of 0.05 per cent based on cobalt. Although the lower limit of this method can be extended as low as 0.001 per cent, the high cost and lack of availability of equipment is a drawback.

Atomic absorption spectrophotometry is one of the best methods available for determining nickel in cobalt. Levels of 2 to 20 ppm nickel have been determined using the 2320 Å line (11). Better accuracy and precision are obtained using the 3414 Å line since there is less noise at this wavelength; however the lower limit then is 30 ppm. This method is becoming much more accepted as new and relatively inexpensive instruments are being developed.

Neutron activation analysis has been used to determine as little as 8 ppm nickel in cobalt (12). However a large neutron flux and long irradiation times are required. The drawbacks of this method are lack of availability of reactors, long times involved, and the need for expensive equipment.

In light of the preceeding discussion, the problem of determining nickel traces in cobalt still suffers from the lack of a method which combines reasonable speed with good accuracy, uses commonly available and

inexpensive equipment, and is sufficiently sensitive to determine very low levels of nickel. The lack of such a method was of little consequence until a few years ago. However recent years have seen the development of a whole new area of science and technology dependent upon high purity materials. With this development in technology, trace analysis has become a major concern of analytical chemists. In light of current needs and with anticipation of those of the future, the development of a facile method for determining traces of nickel in cobalt seems timely.

CHAPTER II

EQUIPMENT AND CHEMICALS*

Laboratory Equipment

Spectrophotometers

All absorbance curves were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer. All quantitative analytical absorbance measurements were made with a Bausch and Lomb Spectronic 20 spectrophotometer.

Phototitrator

The Flaschka-Butcher phototitrator (15) was used with a modified light source. A General Electric #209 lamp was used with a power source of two 6-volt storage batteries connected in parallel.

pH Meter

All pH measurements were made with a Beckman Zeromatic II pH meter. The meter was standardized with a Beckman standard buffer of pH 9.18.

Glassware

The usual glassware such as beakers, flasks, separatory funnels, etc. were used as needed. For volumetric measurements class A volumetric glassware was used exclusively and without additional calibration.

Chemicals

Water

Deionized water was used exclusively.

*Equipment and chemicals for all work in Chapters III through VI are listed herein.

Murexide

J. T. Baker reagent grade murexide powder was used exclusively.

Nickel

J. T. Baker reagent grade nickel shot was used. An amount of 0.3 g was dissolved in a minimum amount of 1:1 nitric acid and boiled to expel oxides of nitrogen. The solution was diluted to 500 ml. This stock solution was standardized by titration with 1.00×10^{-2} F EDTA as follows:

To aliquots of the nickel solutions, NH_3-NH_4Cl pH 10 Buffer was added dropwise until all precipitates, which formed, redissolved. Three or four drops excess buffer were added, followed by dilution and addition of murexide. The resulting solutions were titrated to a visual end point. The solution, thus standardized, was 9.66×10^{-3} F in nickel. Test solutions were prepared from this stock by serial dilution.

Cobalt

Cobalt sponge of 99.999% proclaimed purity from K&K Laboratories was used. Solutions 0.1 F in cobalt were prepared by dissolving 2.9 grams of this metal in a minimum of 1:1 nitric acid. The solution was boiled and diluted to 500 ml.

Disodium (Ethylenedinitrilo)tetraacetic Acid Dihydrate (EDTA)

J. T. Baker reagent grade disodium EDTA was used. An amount of 37.225 grams was dissolved in water. A few pellets of sodium hydroxide were added to hasten dissolution. The resulting solution was diluted to the mark in a 1-liter flask, and aliquots were taken and standardized against 0.1000 F zinc solution. The concentration of the EDTA solution was 0.1001 F. From this stock solution, more dilute solutions were pre-

pared by serial dilution.

Ammonia

E. I. DuPont de Nemours concentrated aqueous ammonia was used.

Hydrogen Peroxide

Mallinckrodt Chemical Works "analytical reagent" 3% hydrogen peroxide, stabilized with acetanilid, was used.

Fisher Scientific Company reagent grade 30% hydrogen peroxide was used.

Acids

E. I. DuPont de Nemours concentrated nitric, hydrochloric, and sulfuric acid were used.

Zinc Standard Solution

A standard 0.1000 F zinc solution was prepared by dissolving 6.538 grams of J. T. Baker reagent grade zinc granules in a minimum amount of 1:1 nitric acid. The solution was boiled to expel oxides of nitrogen and diluted to exactly one liter.

Salts for Ionic Strength Investigations

J. T. Baker reagent grade ammonium chloride, sodium chloride, sodium nitrate, potassium nitrate, and potassium chloride were used. Merck Co. dried powder sodium sulfate was used.

Sucrose

Certified reagent grade sucrose from Fisher Scientific Company was used.

Ca-EDTA

A solution of 0.20 F calcium chloride was prepared from J. T. Baker reagent grade salt. A solution of 0.20 F EDTA was prepared from

J. T. Baker reagent grade disodium salt. One hundred milliliters of each of these solutions were mixed. A few drops of the 0.20 F $CaCl_2$ were added in excess to assure that all EDTA was complexed.

1-(2-Pyridylazo)-2-Naphthol (PAN)

Certified reagent grade PAN from Fisher Scientific Company was used. A 0.01 F solution was prepared by dissolving 0.622 g of the solid in enough 95 per cent ethanol to make a total volume of exactly 250 ml. Warming the mixture hastens dissolution.

Tiron

Fisher Scientific Company certified reagent grade tiron was used.

Potassium Iodide

J. T. Baker U.S.P. grade potassium iodide was used.

Buffer pH 5

J. T. Baker reagent grade sodium acetate was used to prepare an approximately 1 F solution which was brought to pH 5 by addition of hydrochloric acid.

Thiourea

J. T. Baker reagent grade thiourea was used.

Tartaric Acid

J. T. Baker reagent grade d-tartaric acid was used.

Ascorbic Acid

Fisher Scientific Company certified reagent grade l-ascorbic acid was used.

Ammonium Chloride

J. T. Baker reagent grade ammonium chloride was used.

Other Metal Salt Solutions

J. T. Baker reagent grade metal salts were used to prepare aqueous solutions as needed. If the salt is one which undergoes hydrolysis, a few drops of nitric acid are added.

Chloroform

Fisher Scientific Company, N. F. grade chloroform was used. The chloroform was washed with dilute aqueous hydrochloric acid to remove cations prior to use. Following the acid wash the chloroform was washed in dilute aqueous ammonia.

Alcohol

U. S. Industrial Chemical Company 95 per cent ethanol was used throughout.

Storage of Solutions

All chelon and indicator solutions, all alkaline solutions, and all dilute (0.001 *F* or less) metal ion solutions were stored in polyethylene bottles.

CHAPTER III

PHOTOMETRIC TITRATION OF NICKEL TRACES WITH EDTA

Introduction

Some of the best methods for the determination of nickel are titrimetric ones. The EDTA titration is especially good. It yields an extremely sharp end point and has been applied successfully to even very small amounts of nickel. Unfortunately neither this titration nor any other can be employed in the presence of cobalt unless some drastic measures are taken. The cobalt is either cotitrated or it interferes in other ways. It should, however, be possible to improve the situation by application of appropriate masking because there are reactions which are quite different for nickel and cobalt. Especially, the possibility of oxidizing cobalt to the trivalent state in which it forms extremely stable or robust complexes should offer some possibilities for a solution of the problem. Nearly all of the cobalt(III) complexes are intensely colored and thus a visual indication of the titration should be impossible. Of instrumental end points direct potentiometry could not be applied because no workable redox couple exists for the nickel. Amperometry could hardly be applied because of the polarographic waves resulting from the masked cobalt and possibly from other species in solution. The best choice seemed to be a photometric end point because there are many cases in the literature where this technique was applied to titration of minute amounts of metals with very satisfactory results.

When looking for an appropriate masking agent ammonia seemed to be a likely choice. The nickel-ammine complexes react with EDTA even in strongly ammoniacal medium. However, the cobalt(III) hexamino complex is inert towards EDTA as has been reported by Babaeva and coworkers (13). The ammine complexes can be obtained by oxidizing the cobalt(II) in an ammoniacal medium. The most convenient oxidant seems to be hydrogen peroxide.

Preliminary Investigations

A systematic investigation of ammoniacal solutions containing nickel, cobalt, H_2O_2, and EDTA was begun.

Spectral curves (Figure 1) revealed that a titration to a self-indicated end point was not feasible for two reasons. First, the molar absorptivities of both the ammine complex and the EDTA complex of nickel are too small for this purpose. Second, the absorbance curves of the two complexes do not differ sufficiently. Therefore an indicator for the nickel was necessary.

Indicators (Murexide)

In solutions containing a small amount of NH_3-NH_4Cl buffer of pH 10 several indicators were investigated, including SNAZOX, Brompyrogallol red, pyrocatechol violet, pyrocatecholphthalein, PAN, PAR, Chromazurol-S, and murexide. The majority of the indicators proved to be unsuitable for one or both of the following reasons. First, the spectral curves of the metallized and the unmetallized indicator were either not sufficiently different to allow selection of an appropriate operating wavelength, or such a wavelength was in the region of the intense background absorbance due to the ammine complex of cobalt(III). Examples of these types of in-

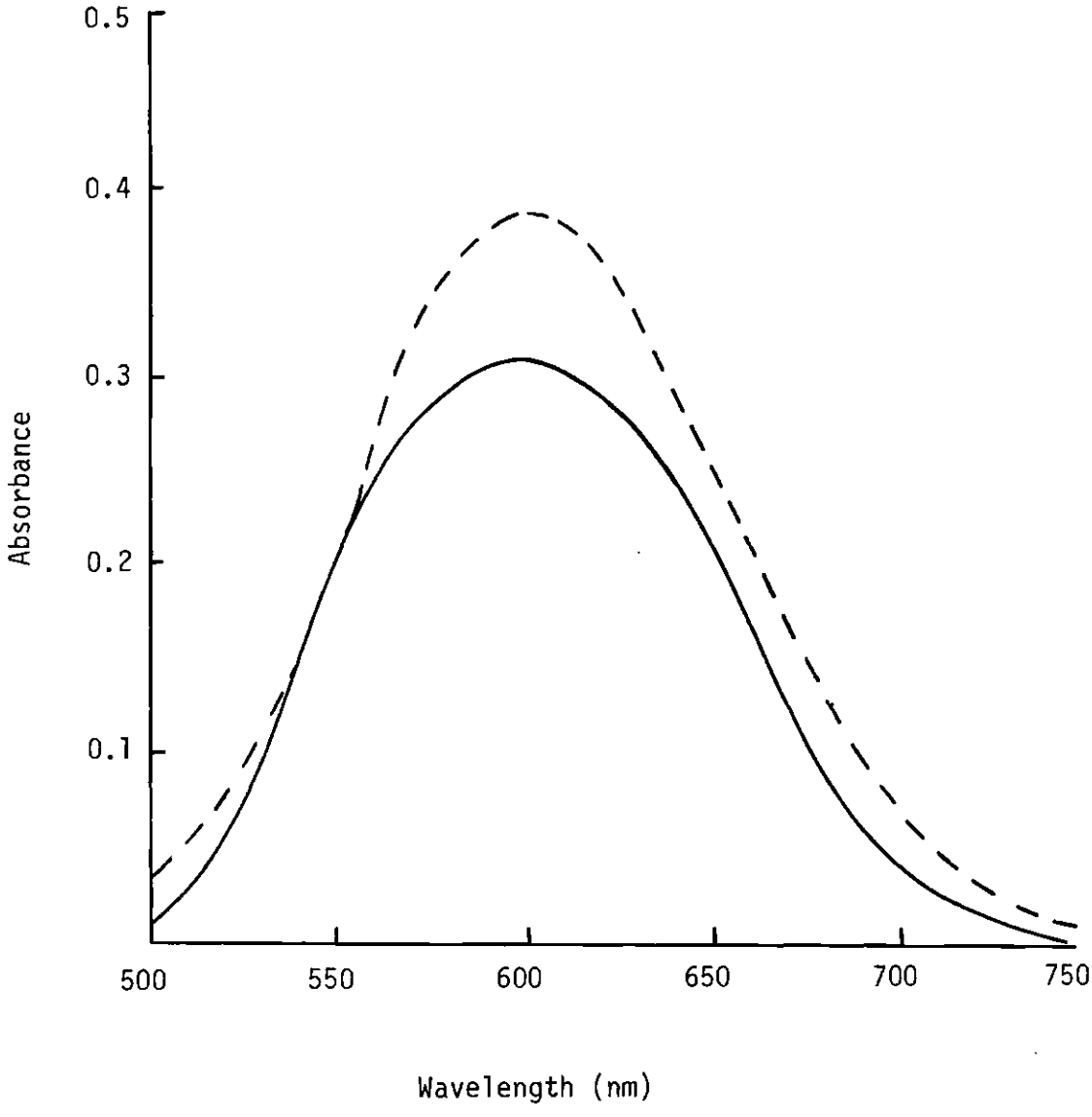


Figure 1. Spectral Curves of 0.05 F Ni-EDTA (---) and 0.05 F $Ni(NH_3)_6^{2+}$ (——) in NH_3-NH_4Cl Buffer pH 10.

dicators include SNAZOX, Brompyrogallol red, PAR, Chromazurol-S, pyrocatechol violet, and pyrocatecholphthalein. Second, some nickel-indicator complexes reacted only very slowly with the titrant, as, for example the nickel-PAN complex. Of all the indicators investigated murexide was the only one which gave promise as being suitable for the titration procedure.

Figure 2 shows the absorbance curves of the nickel-murexide complex (curve A) and of unmetallized murexide (curve B). The curves of the yellow nickel-murexide and of the violet unmetallized murexide differ sufficiently that an appropriate wavelength can be selected for a photometric titration. In addition the nickel-murexide complex reacts readily with EDTA. Therefore on the basis of its behavior in the preliminary investigations, murexide was chosen as the indicator.

Masking of Cobalt

Since the hexammine complex of cobalt(III) was reported (13) to be unreactive toward EDTA, the initial investigations were directed toward that complex. Although the complex can be prepared by oxidation of cobalt(II) with hydrogen peroxide in ammonical medium (14), several problems arose when attempts were made to apply these reactions in the development of the analytical method.

A catalyst is needed in order to achieve sufficiently rapid formation of the cobalt(III) hexamine complex. Charcoal is commonly used for this purpose but its presence in a solution to be titrated photometrically is obviously prohibited. Thus the feasibility of filtering off the charcoal was investigated. However when solutions containing nickel and charcoal were filtered, the filter washed, and the filtrate subsequently titrated with EDTA, the nickel found was sporadically lower

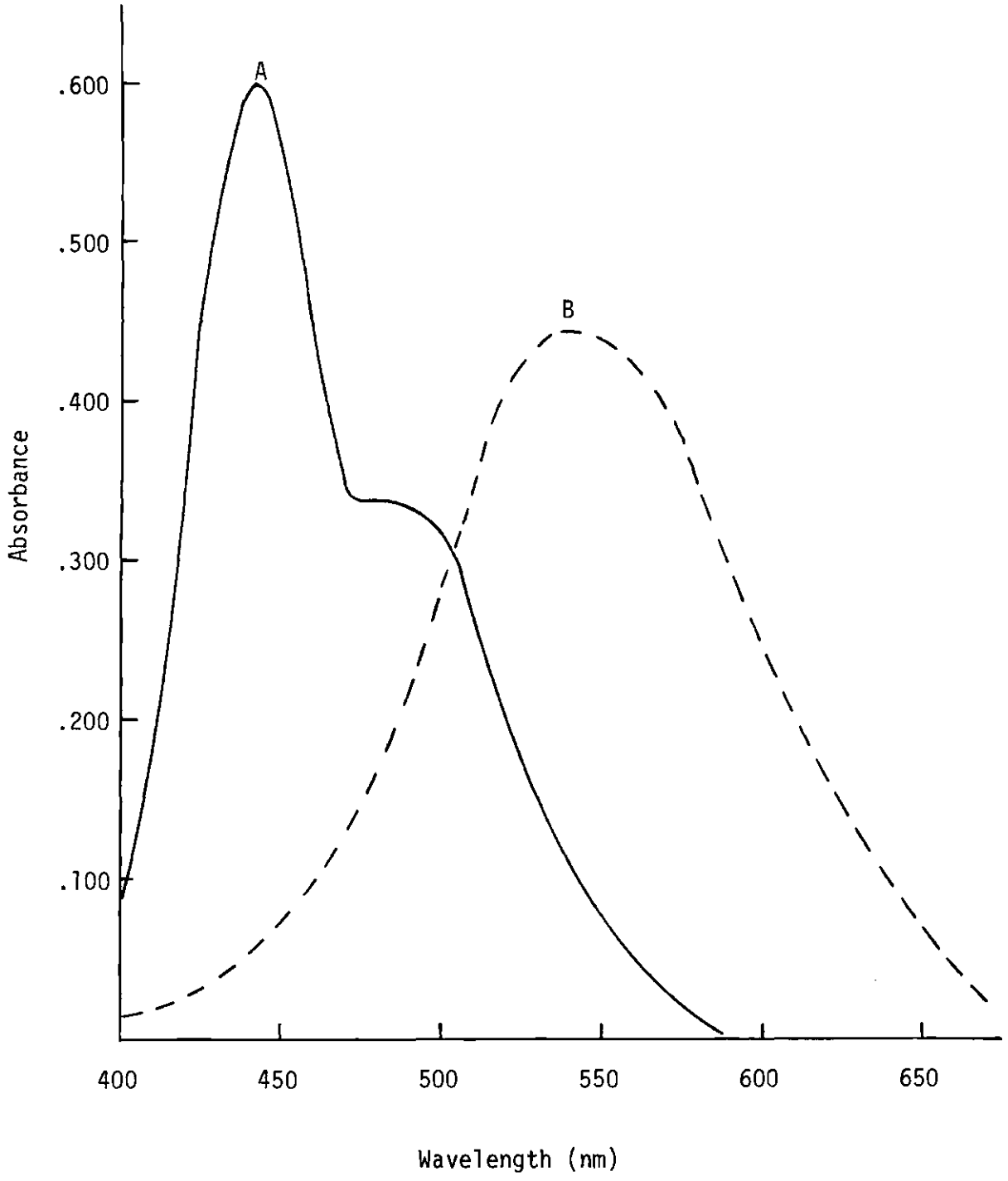


Figure 2. Spectral Curves of the Ni-Murexide (——) and Free Murexide (---) in Aqueous Ammonia.

than that added.

High concentrations of ammonium salts are necessary for the complete transformation of all the cobalt present to the hexammine complex. In the absence of ammonium salts the red pentammine complex is formed exclusively. The requirement of high ammonium salt concentration presented an unexpected problem. Experiments revealed that even with moderate amounts of ammonium salts present the yellow nickel-murexide complex did not form, and if originally formed, it decomposed upon addition of salt. Not only ammonium salts but any salt had the same effect, which is due to high ionic strength and is dealt with in some detail in Chapter IV.

In addition to the two problems already discussed, the low solubility of the hexammine cobalt(III) salts caused difficulties because it limited the permissible concentration of cobalt to a level too low to be of practical value. The possibility of using the hexammine complex for masking appeared quite nice initially, but in light of the investigations discussed above, it proved to be out of the question. During the experiments some hints had been obtained that the pentamine complex might serve the purpose much better, and investigation in this direction was initiated.

As was previously stated, when cobalt(II) is oxidized by hydrogen peroxide in ammoniacal solutions containing no ammonium salts, the red pentammine complex of cobalt(III) is formed without requiring a catalyst. Therefore, studies were made to determine if the pentammine complex could effectively mask cobalt against reaction with EDTA in the titration procedure. Cobalt(II) was oxidized by hydrogen peroxide in ammoniacal solution containing no ammonium salts or catalysts as outlined by Bjerrium and McReynolds (14). The red pentammine complex of cobalt(III) which

forms under these conditions shows an absorbance maximum (Figure 3) very near that of uncomplexed murexide in ammoniacal medium. Therefore a photometric titration could be performed at a wavelength at which the yellow nickel-murexide complex absorbs.

After establishing that the pentammine complex of cobalt(III) could be formed quite readily in ammoniacal solution, attempts were made to titrate nickel in presence of cobalt at a wavelength of 442 nm using the semi-immersion phototitrator described by Flaschka and Butcher (15). It became immediately obvious that the phototitrator would have to be modified to be useful for this titration.

Modifications of the Phototitrator

The exciter lamp of the Flaschka-Butcher phototitrator is a #222 miniature lamp rated at 2.2 volts and 0.25 amperes. Its power is supplied by a 4-volt lead-acid storage battery and is regulated by a rheostat. This lamp provides an extremely stable light source and is quite satisfactory at wavelengths greater than about 500 nm. However the lamp does not emit sufficient blue light to be useful at the wavelength of 442 nm, and a different light source had to be found.

A very exhaustive search of available lamps that would be compatible with other design features of the phototitrator showed only the General Electric #209 miniature lamp to be totally satisfactory. The lamp has a B-6 bulb, a single contact bayonet base, and is rated at six volts and 1.78 amperes. Two six-volt storage batteries, connected in parallel to provide stability against the relatively high current draw, were used as the power source. The lamp housing was modified to accommodate the #209 lamp, and in addition several socket adapters were built

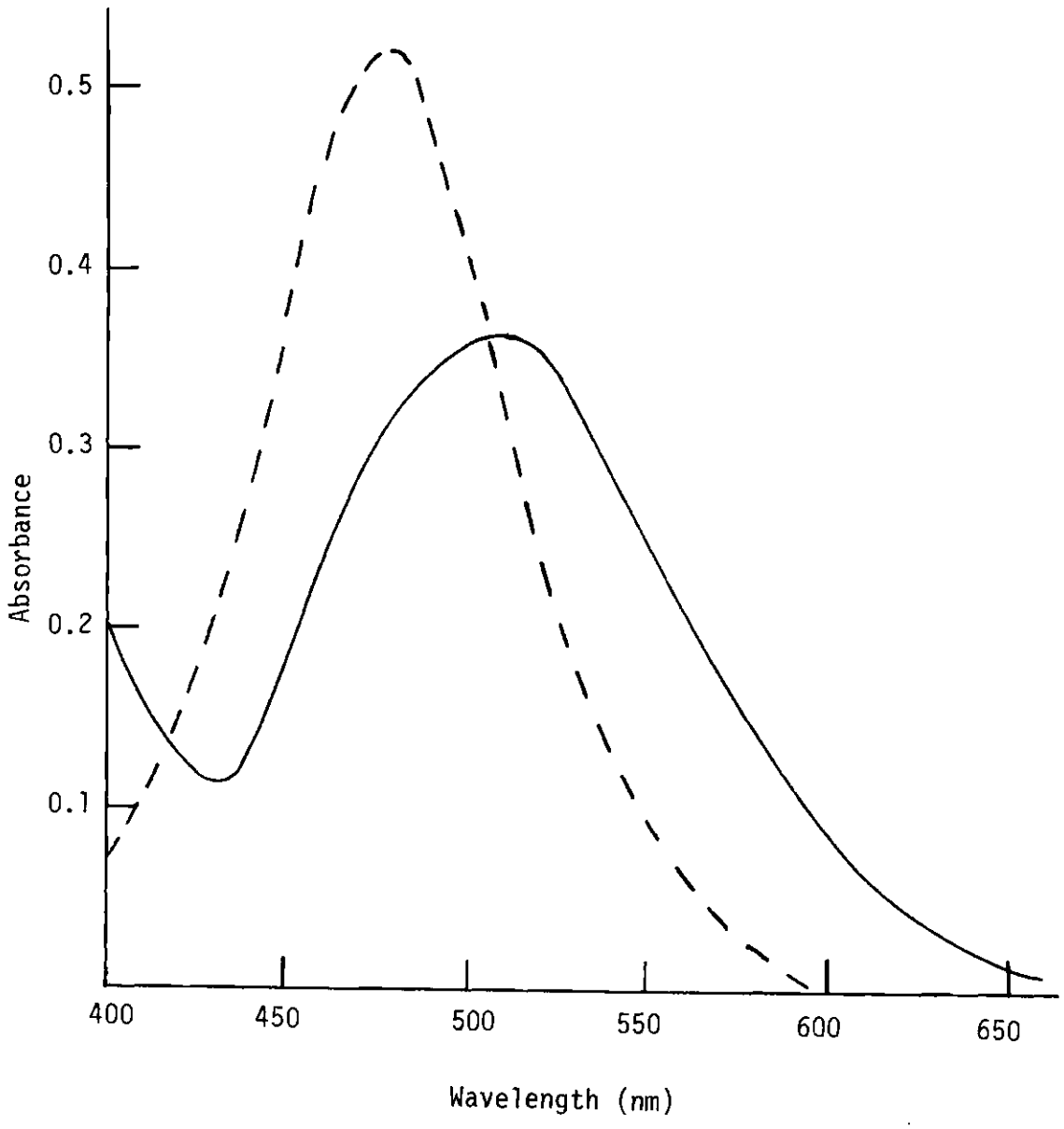


Figure 3. Spectral Curves of Cobalt-Ammonia Complexes: $Co(NH_3)_5OH^{2+}$ (——), $Co(NH_3)_6^{3+}$ (---).

to permit use of a wide range of lamps for future operations.

An interference filter transmitting at 442 nm, in combination with a Baird-atomic-440 blocking filter was used as the monochromating device.

Preliminary Titrations

The initial titrations were unsuccessful because the transmittance of the solution changed continusously thus making the location of the end point impossible. At first this drift was thought to be caused by the decomposition of the indicator. Murexide in the free, unmetallized form is known to undergo hydrolysis in aqueous solution, although only slowly in alkaline media. Unmetallized murexide was present in the solution since excess indicator was added to assure that all nickel was complexed. Because the tail of the absorbance band of the free murexide passes through the operating wavelength, the drift was thought to be due to the hydrolysis of the indicator. To determine whether or not hydrolysis caused the drift was a simple and straightforward matter.

Ammoniacal solutions containing only nickel, a few drops of aqueous ammonia, and a slight excess of murexide were titrated with EDTA and no drift was observed. Data points representing the absorbance after incremental addition of EDTA were plotted and straight-line plots were obtained. These observations suggested that the drift was not caused by the indicator and, therefore, must be caused by the cobalt-ammonia complex.

In light of these observations solutions containing only the freshly prepared pentammine complex of cobalt(III) were placed in the titration vessel and the transmittance was monitored with the galvanometer. No titrant was added. A drift in the direction of increased transmittance was observed as before. Having established that the drift was due to a change

in the cobalt-ammonia complex, absorbance curves were run on the system in an effort to determine the exact cause and to determine the feasibility of controlling the system. The results are outlined below.

Absorbance curves were run periodically on the freshly prepared cobalt-ammonia solutions between 400 nm and 700 nm. The red solutions showed an absorbance maximum at 510 nm, indicating probable presence of $Co(NH_3)_5OH^{2+}$, as is seen in Figure 3, but the solutions showed some absorbance at the shorter wavelength at which the titration is carried out (442 nm). The absorbance at 442 nm was observed to decrease as the solutions were allowed to stand for a period of time, and the absorbance reached a constant value only after several hours. When the absorbance had reached a constant value at 442 nm, the solution was placed in the titration vessel and the transmittance was observed with a galvanometer as discussed previously. No drift was observed on the galvanometer. At this point a small amount of nickel could be titrated to a satisfactory end point. In light of these observations the following explanation is given for the drift.

When ammonia is added to a solution of cobalt(II) ions, the hydrous oxide initially precipitates, and the precipitate redissolves upon addition of excessive amounts of ammonia to form a yellow-brown solution containing the hexammine complex of cobalt(II). The solution shows considerable absorbance at 442 nm. When hydrogen peroxide is added to the above solution, the solution effervesces and slowly changes color from yellow-brown to red. When the effervescence ceased and when no further color change could be detected by the eye, the spectral curves were run on the solutions. Although the formation of the red pentammine complex

of cobalt(III) from the yellow-brown complex of cobalt(II) appeared to the eye to be complete, the reaction was in fact not complete for several hours as was shown by the spectral curves. To further substantiate this explanation a drop of 0.1 formal EDTA was added to a freshly prepared solution of the pentammine complex of cobalt(III), and the absorbance at 442 nm immediately reached a constant value. The yellow-brown hexammine complex of cobalt(II) reacts readily with EDTA to give the red EDTA complex of cobalt(II). Following this observation, a large amount of EDTA was added to the solution to determine the effect of excess EDTA on the pentammine complex of cobalt(III). No further change was observed in the absorbance curve of the pentammine complex even after the solution was allowed to stand for a period of fifteen minutes. It was, therefore, concluded that the pentammine complex of cobalt(III) would not react with EDTA in a titration procedure, since only after the endpoint would the cobalt complex be exposed to "free" EDTA for longer than a few seconds at most. Therefore to make the oxidation and complexation process applicable as a masking aid would require only that a technique could be developed to make the oxidation reaction and the formation of the pentammine complex complete and rapid enough to be useful in the analytical method. Provided the criteria of speed and completeness of reaction could be realized in the masking reaction, the method for the determination of nickel in cobalt should be a straightforward development. The procedure would require three main steps.

First, hydrogen peroxide would be added to an ammoniacal solution containing cobalt and nickel. After the oxidation process and the formation of the pentammine complex were complete, murexide would be added

to form the yellow nickel-murexide complex. The resulting solution would be titrated photometrically at a wavelength of 442 nm. The absorbance at incremental addition of EDTA would be recorded, and the endpoint of the titration would be determined from a graph. Since cobalt would be masked as the pentammine complex, the method should be applicable to the determination of nickel in presence of large amounts of cobalt. With the preliminary investigations in mind, studies were directed toward development of a workable procedure.

Development of the Analytical Method

All aspects of the procedural steps outlined above were studied in detail. First it was necessary to determine the optimum conditions for forming the ammine complex. Preliminary investigations had shown that when ammoniacal solutions containing cobalt were treated with hydrogen peroxide the cobalt was rendered inactive against reaction with EDTA. However to achieve this inactivity it was necessary to let the solution stand for several hours. This observation suggested heating as a possibility of speeding up the reaction to make the masking approach feasible for the analytical method.

Ammonia and hydrogen peroxide were added to solutions containing cobalt, and the solutions were heated on a hot plate for various lengths of time. After cooling the solutions to room temperature, spectral curves were taken and compared to the curves obtained previously on solutions which were allowed to stand for several hours.

The curves were examined in the area of the titration wavelength (442 nm) to determine whether the solution was still changing in composi-

tion or whether the reaction had already gone essentially to completion. In addition the shape of the curve and the peak maximum were examined to help assure that the desired complex was formed. The solutions also were subjected to simulated titration conditions to see whether the above mentioned drift persisted. As was expected heating the solutions greatly reduced the time necessary to achieve completeness of the reaction, but to establish the optimum heating time and temperature several side effects of the heating had to be considered.

Depending on temperature and heating time losses of ammonia are encountered. Furthermore, ammonia and hydrogen peroxide react with each other. The extent of this reaction increases with increasing temperature and losses of oxidant as well as complexing agent are the consequences. In addition temperature accelerates the spontaneous decomposition of hydrogen peroxide, a reaction which is catalyzed further by heavy metal ions. Fortunately, this decomposition is not too serious because one of the decomposition products is oxygen, which is also quite effective in the oxidation of cobalt(II) to cobalt(III). However, at elevated temperatures the oxygen escapes quite rapidly and a decrease in concentration of the oxidant results.

From a series of experiments it was found that the best balance among all the diverse effects and factors was achieved as follows.

The solutions were heated in a water bath which provided better uniformity and control of the temperature. The localized "hot spots" encountered when working on a hot plate had a bad influence and should be avoided. A temperature of 70°C proved optimum. The solution remained in the water bath for seven minutes and was then removed and allowed to

stand until it cooled to room temperature. Thus the actual exposure to elevated temperature was longer than seven minutes. The solution was made very strongly ammoniacal and the hydrogen peroxide was added in two equal portions. One portion was added before the vessel was placed in the water bath. Addition of the second portion was made after five minutes of heating. The split addition assured that towards the end of the warming period still enough oxidant was present to achieve complete oxidation. Solutions containing up to 180 mg of cobalt were treated in this manner and upon investigation the cobalt was found to be completely masked against EDTA. The method is effective for masking much higher amounts of cobalt as will be shown in Chapter V. The restriction to 180 mg here, however, results from the fact that with higher amounts of cobalt the phototitrator could not be set to 100 %T because of the high background color of the solution.

Solutions containing cobalt and known amounts of standard nickel solution were prepared as outlined above and were transferred to the titration vessel. The transmittance was adjusted to 100%. Murexide was then added in an amount more than sufficient to complex all the nickel present. Because of the poor stability of murexide solutions the indicator was added either as the pure solid or as a finely ground 2%-mixture with sucrose. The actual amount for each individual solution is determined in the following manner. The indicator is introduced in small portions and the deflection of the galvanometer mark is observed. Initially each portion causes a large deflection as the yellow, strongly absorbing, nickel-murexide is formed. When all nickel is transformed to the murexide complex, further additions cause only a very small deflection

of the galvanometer mark, since free murexide absorbs only slightly at the selected wavelength. Once the movement of the mark becomes slight, sufficient murexide has been added and the solution is ready for titration.

In the first titrations performed on such solutions the amount of nickel found was sporadically higher than the amount actually taken. At first the high results were thought to be due to cotitration of traces of cobalt, which remained as the hexammine complex of cobalt(II) but, due to the low absorptivity of the complex, could not be detected by the method described previously. To determine whether or not traces of unmasked cobalt caused the high results, several identical solutions were prepared according to the established procedure, and were allowed to stand for various lengths of time up to six hours before being titrated. If traces of cobalt remained unmasked, the amount should have decreased as the standing time became longer, and a regular decrease in the amount of EDTA needed to reach an end point should have resulted. Such was not the case.

However during these careful investigations, the titration curve was observed to have two changes of slope. This fact previously had gone unnoticed because larger increments of titrant were taken in the initial titrations, and only three or four points before and after the endpoint were plotted.

Figure 4 shows a characteristic titration curve. Two breaks strongly indicate the titration of at least two species. If the difference between the two breaks (A and B) was taken as the basis for the calculation, results for nickel were correct. Further investigations showed that the titrant required to reach the first break is consumed by calcium which is present as an impurity, and which is introduced predomi-

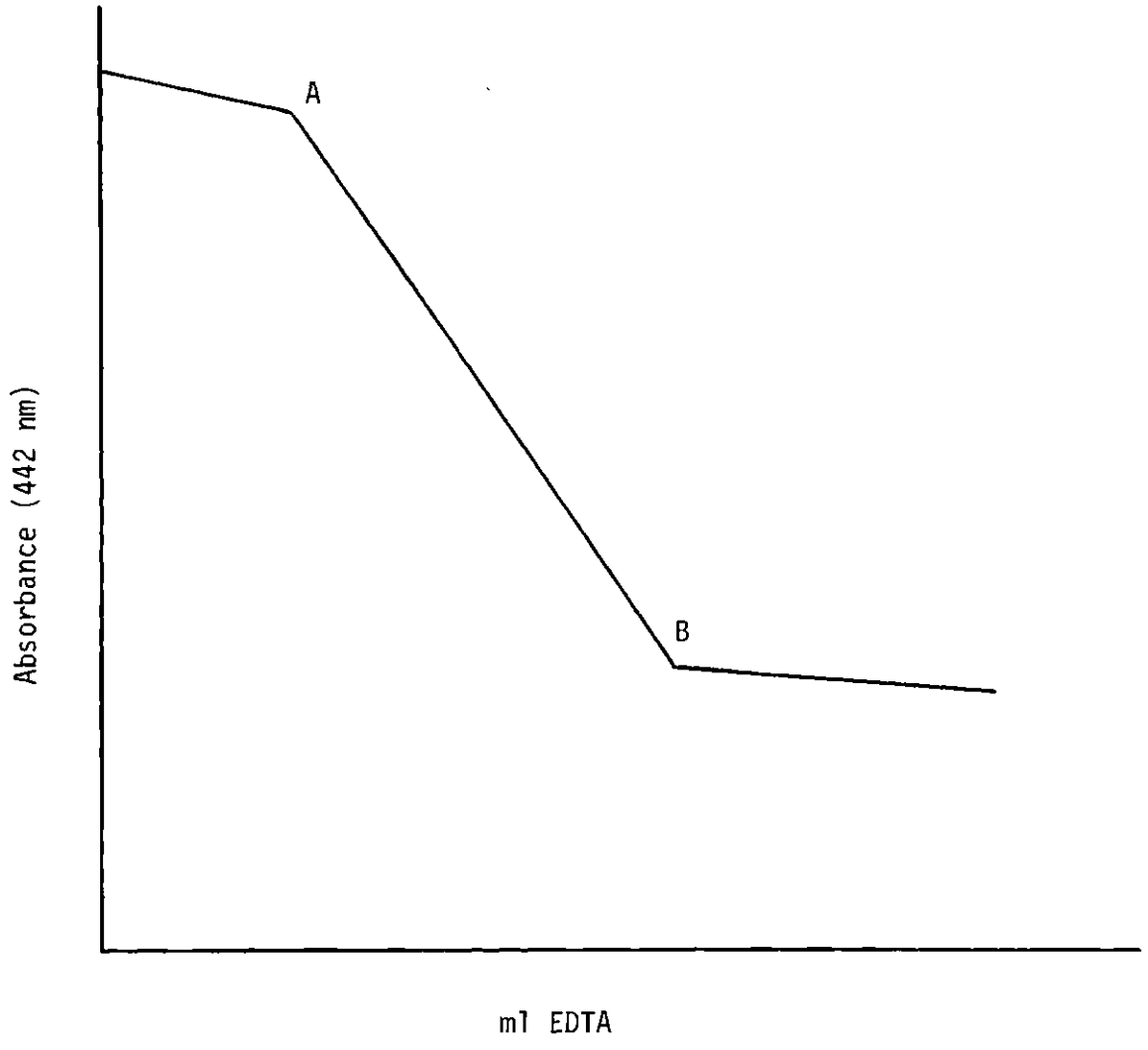


Figure 4. Characteristic Curve Obtained for the Photometric Titration of Nickel-Murexide with 10^{-3} F EDTA in Aqueous Ammoniacal Medium.

nately with the aqueous ammonia.

With all of the original difficulties cleared up and explained, it was possible to concentrate on the final development of the most practical approach for the method. The optimum procedure is outlined stepwise immediately below.

Procedure

1. Dissolve, in a 250-ml beaker, an amount of sample containing between 17 and 60 µg nickel (Notes a and b).

2. Add slowly, while stirring vigorously, 15 ml of concentrated aqueous ammonia. The solution should be clear and yellow-brown when all ammonia has been added. If a turbidity persists after stirring for a few seconds, add more ammonia to clear the solution.

3. Measure a volume of 3% hydrogen peroxide such that 0.25 ml is taken for each milligram of cobalt present. Add one half of this volume to the solution from step (2). Cover the beaker and place it in a water bath kept at 70 ±5°C for five minutes (Note c).

4. Wash down the watch glass and the sides of the beaker with a small amount of water from a wash bottle (Note d). Add the second portion of 3% hydrogen peroxide and leave in the water bath for two additional minutes.

5. Remove the solution from the water bath and allow it to stand until it has reached room temperature. Add approximately one half milliliter of triethanolamine if iron, manganese, and aluminum are to be masked.

6. Transfer the solution, quantitatively, to the vessel of the phototitrator, dilute to approximately 120 ml, and adjust the light

probe to a path length of one to three centimeters (Note e).

7. Set the transmittance to 100%, or for solutions with high absorbance backgrounds, set it as close to 100% as possible (Note f).

8. Add murexide indicator in small increments, while stirring, and observe the deflection of the galvanometer after each addition. When the deflections become very slight, cease adding indicator (Note g).

9. Add 5 ml of 0.1 F Ca-EDTA and allow the solution to stand for six minutes (Note h).

10. Titrate with 10^{-3} F EDTA employing 0.05-ml increments.

11. Record the transmittance at each increment of titrant and plot the titration curve (Note i).

12. Subtract the volume at the first break from the volume at the second break in the curve and use this difference as the basis for the calculation.

Notes

a. Dissolve cobalt metal in a minimum amount of either warm 1:1 nitric acid or warm concentrated (12 F) hydrochloric acid. Dissolve salts and other compounds as is appropriate.

b. The cobalt pentammine complex produces such an intense absorbance background that it becomes impossible to set the initial transmittance high enough to be practical when a certain cobalt concentration is reached. As a consequence there is a limit in the amount of sample that can be handled, and that limit depends on the instrumental set-up.

c. Inconsistently high results were obtained if the temperature was allowed to go to 80°C even for a short period of time.

d. During the oxidation process the solution effervesces vigorously, and considerable spattering occurs. The spattered droplets must be washed back into the oxidizing medium. It is desirable that the total solution volume after final addition of hydrogen peroxide is no greater than about 80 ml.

e. The exact path length necessary depends upon both the nickel concentration and the total amount of cobalt present. See the discussion section at the end of the chapter.

f. Gas bubbles form continuously, and care should be taken that they do not collect at the wall of the titration vessel where they may interfere with the light beam. In severe cases interruption of stirring may be required to permit the bubbles to rise to the surface. With an immersion type titrator as employed in the present work the situation is by far less serious. The only requirement is that the stirrer be located close to the tip of the light probe.

g. Usually 2-3 mg of murexide are required. This amount corresponds to a small spatula tip full and can be delivered readily in portions. However it is even more convenient to use a 2% mixture with sucrose of which about 100 to 150 mg are required.

h. If copper is known to be absent from the sample, addition of Ca-EDTA may be omitted. However it is not necessary to predetermine the presence or absence of copper, since addition of Ca-EDTA does not cause harmful effects if copper is absent.

i. The transmittance reading may be either converted to apparent absorbance using a transmittance-absorbance table, or the logarithm of %T/100 may be plotted. Also the %T may be directly plotted on semilog graph paper.

Discussion

Results

Data for the determination of nickel alone and in the presence of cobalt are presented in Table 1. The data show a satisfactory accuracy and precision, and indicate the method to be applicable to the determination of nickel in presence of a ten thousandfold molar excess of cobalt.

The influence of cobalt on the determination of nickel was assessed by adding cobalt to solutions containing known amounts of nickel and then analyzing for nickel according to the outlined procedure. The nickel content of the cobalt added must be so low as to be undetectable in the titration. Unfortunately all common salts investigated proved unsatisfactory; however cobalt metal listed as 99.999% pure from K&K Laboratories was suitable.

Figure 5 shows a curve representing the titration of 28.5 μg of nickel in presence of a four hundredfold molar excess of cobalt. The titration was performed at a pathlength of two centimeters. Total volume of the solution was 120 ml, containing a volume of 15 ml of concentrated ammonia, and a total volume of 10 ml of 3% hydrogen peroxide.

The volume of titrant at A represents calcium (and possibly traces of other impurities) introduced by the reagents. The volume at B represents total titrable metal ions in solutions. The difference between A and B represents nickel.

The Factor Limiting Cobalt to Nickel Ratios

It should be pointed out that ratios of cobalt to nickel are limited to 10,000:1 by the light source of the photititrator and not by the chemistry of the method. The need for a powerful light source has al-

Table 1. Results of Photometric Titrations of Nickel Alone and in the Presence of Cobalt

µg Ni Taken	Ml 1.00×10^{-3} F EDTA			% Difference	Mg Co Added	Mole Ratio Cobalt:Nickel
	Calculated	Found	Difference			
28.5	0.483	0.480	-0.003	0.6	--	
28.5	0.483	0.485	+0.002	0.4	--	
28.5	0.483	0.483	0.000	0.0	--	
28.5	0.483	0.477	-0.006	1.2	--	
57.0	0.966	0.967	+0.001	0.1	--	
57.0	0.966	0.943	-0.023	2.4	--	
57.0	0.966	0.960	-0.006	0.6	--	
57.0	0.966	0.995	+0.029	3.0	--	
28.5	0.483	0.500	+0.017	3.5	6	200
28.5	0.483	0.493	+0.010	2.1	12	400
41.8	0.692	0.631	-0.061	8.8	18	430
34.7	0.591	0.593	+0.002	0.3	18	520
33.0	0.561	0.522	-0.039	7.0	18	550
26.5	0.449	0.455	+0.006	1.3	18	680
43.3	0.739	0.668	-0.071	9.6	30	690
25.1	0.424	0.430	+0.006	1.4	18	720
39.3	0.671	0.718	+0.047	7.0	30	760
38.8	0.663	0.634	-0.029	4.4	30	770
28.5	0.483	0.498	+0.015	3.1	24	800
22.8	0.387	0.395	+0.008	2.1	24	1000
22.8	0.387	0.383	-0.004	1.0	24	1000
22.8	0.387	0.400	+0.013	3.4	24	1000
30.2	0.514	0.509	-0.005	1.0	30	1000
22.8	0.387	0.380	-0.007	1.8	48	2000

Table 1. Results of Photometric Titrationsof Nickel Alone and in the Presence of Cobalt (Concluded).

µgNi Taken	Ml 1.00 x 10^{-3} F EDTA			% Difference	Mg Co Added	Mole Ratio Cobalt:Nickel
	Calculated	Found	Difference			
22.8	0.387	0.396	+0.009	2.3	48	2000
22.8	0.387	0.399	+0.012	3.1	48	2000
22.8	0.387	0.387	0.000	0.0	72	3000
22.8	0.387	0.400	+0.013	3.4	72	3000
22.8	0.387	0.382	-0.005	1.3	96	4000
22.8	0.387	0.460	+0.073	18.9	144	6000
17.1	0.250	0.300	+0.050	20.0	180	10,000

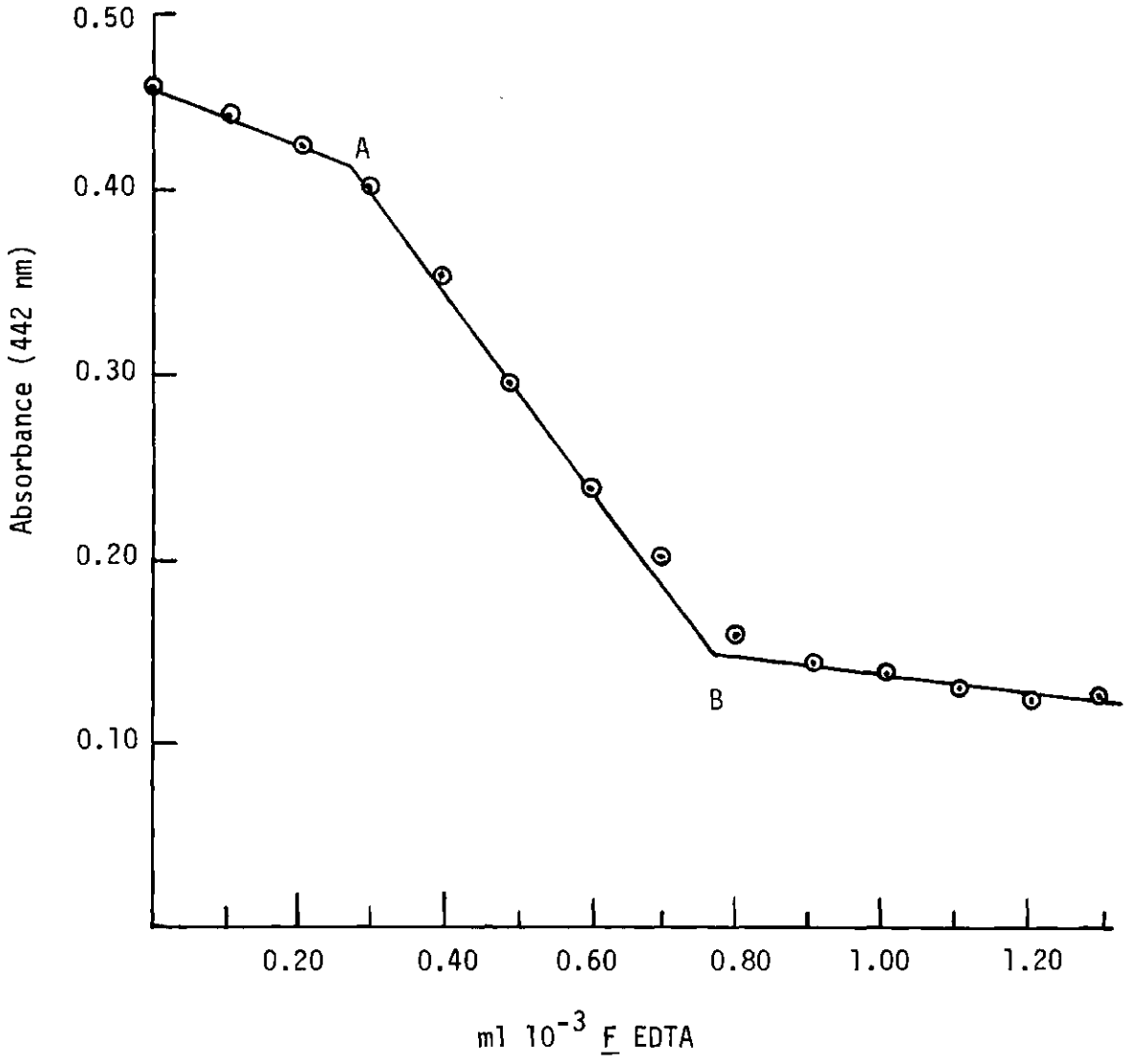


Figure 5. Titration of 0.50 ml of 9.66 x 10^{-4} F Ni^{2+} in Presence of Cobalt. Molar Ratio of Co:Ni is 400:1. (B-A is equivalent to nickel).

ready been discussed, but when large amounts of cobalt are present in a sample this need is even more pronounced. This fact is clearly demonstrated by the curve in Figure 3. Solutions containing large amounts of cobalt produce a very high background absorbance since the absorbance curve "tails" into the operating wavelength of 442 nm. Even with the light source operated at its maximum rating of six volts, the concentration of cobalt was limited to 180 mg in 120 ml of solution. At this concentration the pathlength had to be reduced to one centimeter in order to get sufficient light through the solution to produce an adequately high galvanometer reading. The lower limit of nickel allowable under these conditions was 17.1 µg. The ultimate effect of shortening the pathlength and reducing the nickel concentration is a titration in which the total change in absorbance from the start to the end point is less than 0.100 absorbance units. Consequently a rather flat titration curve results. The situation is further complicated by the necessity of taking the difference between two breaks in the curve to obtain the volume of titrant equivalent to the nickel. Therefore it is suggested that with improvement of the light source higher cobalt to nickel ratios could be tolerated.

Interferences

The necessity of maintaining a rather low ionic strength, as previously mentioned, makes masking of foreign ions against either precipitation or reaction with EDTA somewhat difficult. Most common masking agents dissociate strongly in solution and, to be effective, are required in such large amounts that a prohibitively high ionic strength results from their presence in solution. Therefore masking agents are

limited to nondissociating substances and to those strongly dissociating materials which can be effectively used in such low concentrations that the ionic strength is not unduly increased. Fortunately some such masking agents are available. In addition several ions need not be masked since they react with EDTA preferentially over nickel, as for example, calcium mentioned previously, and are included in the "pretitration" portion of the curve. Therefore with masking of some ions and "pretitration" of others, nickel was titrated successfully in the presence of all foreign ions which might be expected to be present in high purity cobalt.

Table 2 shows the results of titration of nickel in presence of these ions. Since nickel is logically expected to be the major contaminant in high purity cobalt, metal to nickel molar ratios no greater than one to one were investigated. Of the metal ions shown in Table 2, iron, manganese, and aluminum are masked by triethanolamine. Chromium(III) reacts with hydrogen peroxide to form the chromate ion which is unreactive toward EDTA. Since these ions are completely masked, supposedly greater amounts of them could be tolerated. However investigation of this supposition was thought to be unnecessary.

Those ions which are "pretitrated" in addition to calcium are cadmium, zinc, lead, and mercury.

Figure 6 shows, as an example of "pretitrated" impurities, the titration of nickel with 10^{-3} F EDTA in presence of lead. The solution titrated contained 0.500 ml of 9.66×10^{-4} F Ni^{2+}, 0.500 ml of 9.8×10^{-4} F Pb^{2+}, and 15.0 ml of concentrated aqueous ammonia. It is noteworthy to compare Figure 6 with Figure 5. Since both solutions contain the same amount of ammonia, the volume of EDTA representing calcium in the preti-

Table 2. Results of Photometric Titration of Nickel in Presence of Cobalt and Other Foreign Metal Ions. (Enough Cobalt was added to each solution to give a Cobalt:Nickel Ratio of 4,000. All other metals are in a M:Ni Ratio of 1:1).

µg Ni Taken	Ml 1.00×10^{-3} F EDTA				Metal Added
	Calculated	Found	Difference	% Difference	
28.5	0.483	0.467	-0.016	3.3	Ca
28.5	0.483	0.501	+0.018	3.7	Cd
28.5	0.483	0.468	-0.017	3.5	Cd
28.5	0.483	0.470	-0.013	2.7	Pb
28.5	0.483	0.486	+0.003	0.6	Pb
28.5	0.483	0.490	+0.007	1.4	Mn(a)
28.5	0.483	0.480	-0.003	0.6	Zn
28.5	0.483	0.462	-0.023	4.8	Zn
28.5	0.483	0.492	+0.009	1.9	Cr
28.5	0.483	0.488	+0.005	1.0	Fe(a)
28.5	0.483	0.600	+0.117	24.0	Cu(b)
28.5	0.483	0.630	+0.147	30.4	Cu(b)
28.5	0.483	0.500	+0.017	3.5	Cu(c)
28.5	0.483	0.477	-0.006	1.2	Cu(c)
28.5	0.483	0.492	+0.009	1.9	Hg
28.5	0.483	0.482	-0.001	0.2	Al

(a) Approximately 0.5 ml triethanolamine added after step five.

(b) No Ca-EDTA added.

(c) 5.0 ml 0.1 F Ca-EDTA was added and was allowed to stand six minutes.

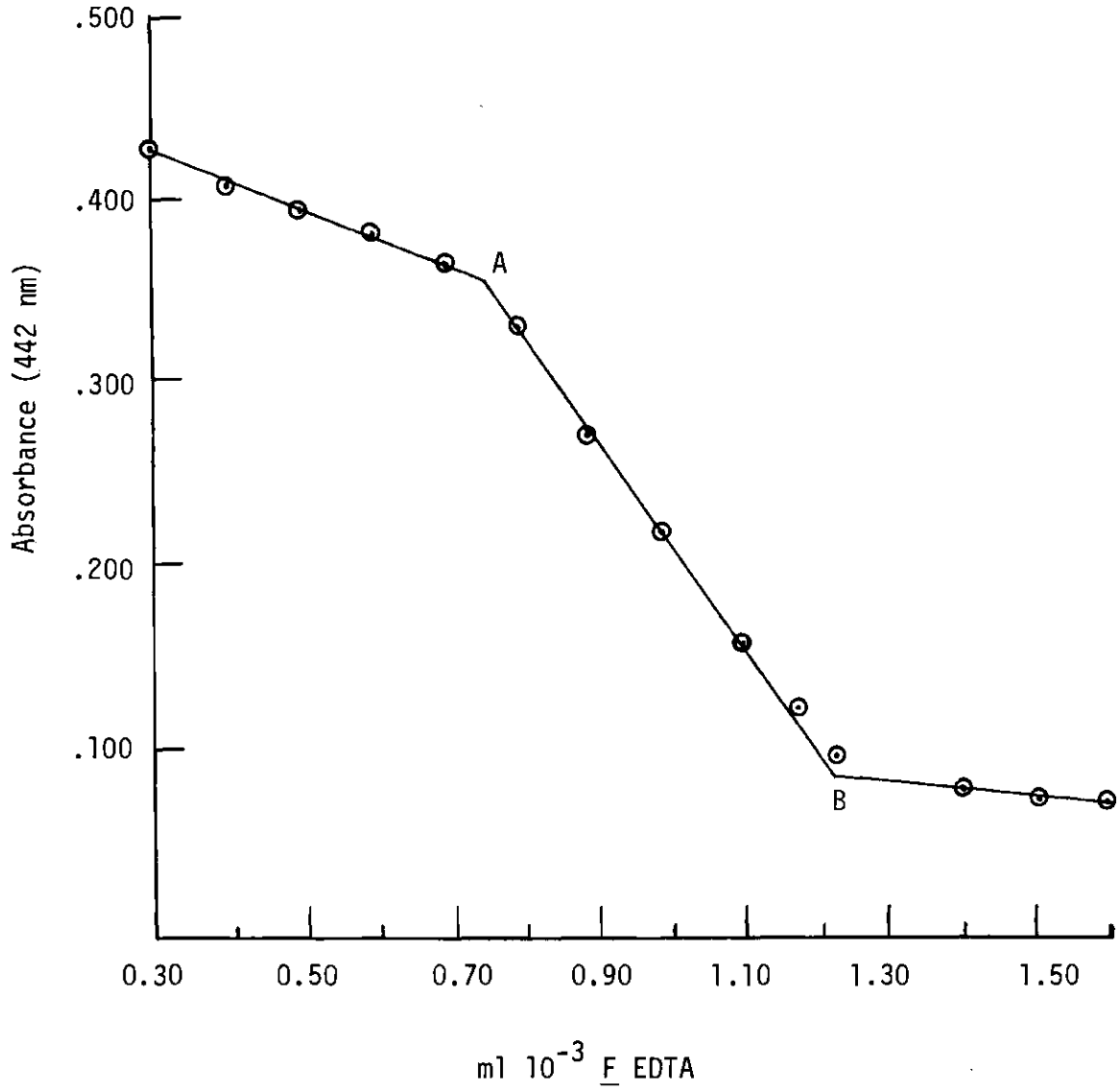


Figure 6. Titration of Nickel in Presence of Lead. Solution Contained 0.50 ml of 9.66×10^{-4} F Ni^{2+}, 0.50 ml of 9.8×10^{-4} F Pb^{2+}.

tration portions of both curves should be equal, for all practical purposes. Subtraction of the volume at point A in Figure 5 from that at point A in Figure 6 gives a value of 0.47 ml of EDTA. The calculated volume of 10^{-3} F EDTA necessary to titrate lead is 0.49 ml. It is suggested that the first portion of the titration curve be used as a guide to indicate total titrable impurities other than nickel in high purity cobalt.

Copper presented a special problem which merits mentioning here. Under all conditions discussed immediately above, copper was at least partially cotitrated with nickel. Several titrants other than EDTA were tried with hope that one of them would preferentially titrate copper as EDTA preferentially titrated the ions already mentioned above. The titrants investigated were DTPA, EGTA, cyclo, and NTA, but none was successful.

A large number of common masking agents for copper was investigated. Some of the compounds tested were cysteine, cystine, tiron and several amines, all of which were unsatisfactory. Although they masked copper they also prevented the reaction between nickel and murexide. Therefore their use is precluded. Copper was successfully handled, however, by addition of Ca-EDTA to the solution after murexide had been added. Copper reacts with the Ca-EDTA to displace calcium from the complex and form Cu-EDTA. The free calcium displaced is then included in the pretitration portion of the curve. It is necessary to have all nickel complexed with murexide prior to addition of Ca-EDTA, since experiments showed that the weaker nickel-hexammine complex, which is present in absence of murexide, also reacted with Ca-EDTA.

Figure 7 shows graphically the results of addition of Ca-EDTA to

solutions of copper and nickel in presence of murexide. To obtain the curves individual solutions of nickel and copper were placed in the phototitrator and murexide was added as in the titration procedure. Five milliliters of 0.1 F Ca-EDTA were added to the solutions and the transmittance was monitored as a function of time. Plot A obtained from the nickel solution shows no change in transmittance after twenty-two minutes, indicating that no reaction occurred between nickel-murexide and Ca-EDTA within this time interval. The copper solution, however, showed an immediate change in transmittance upon addition of Ca-EDTA, and curve B shows the reaction to be complete after about six minutes. At that time the color of the solution was the color of free murexide to the eye. With this knowledge at hand, solutions containing both nickel and murexide were treated with Ca-EDTA for at least six minutes and subsequently were titrated with EDTA. Satisfactory results for nickel were obtained.

Conclusions

The method here developed has shown satisfactory accuracy and precision for the determination of nickel in high purity cobalt. Although investigations here were limited to a nickel level of 0.01% based on cobalt, the chemistry of the method is capable of extension to considerably lower limits with development of a better light source or a more sensitive detector for the phototitrator. It has been demonstrated that the method is applicable in presence of foreign ions most likely to accompany nickel in a sample.

The real value of the method lies in its simplicity. It utilizes inexpensive equipment which is easily operated and easily constructed in

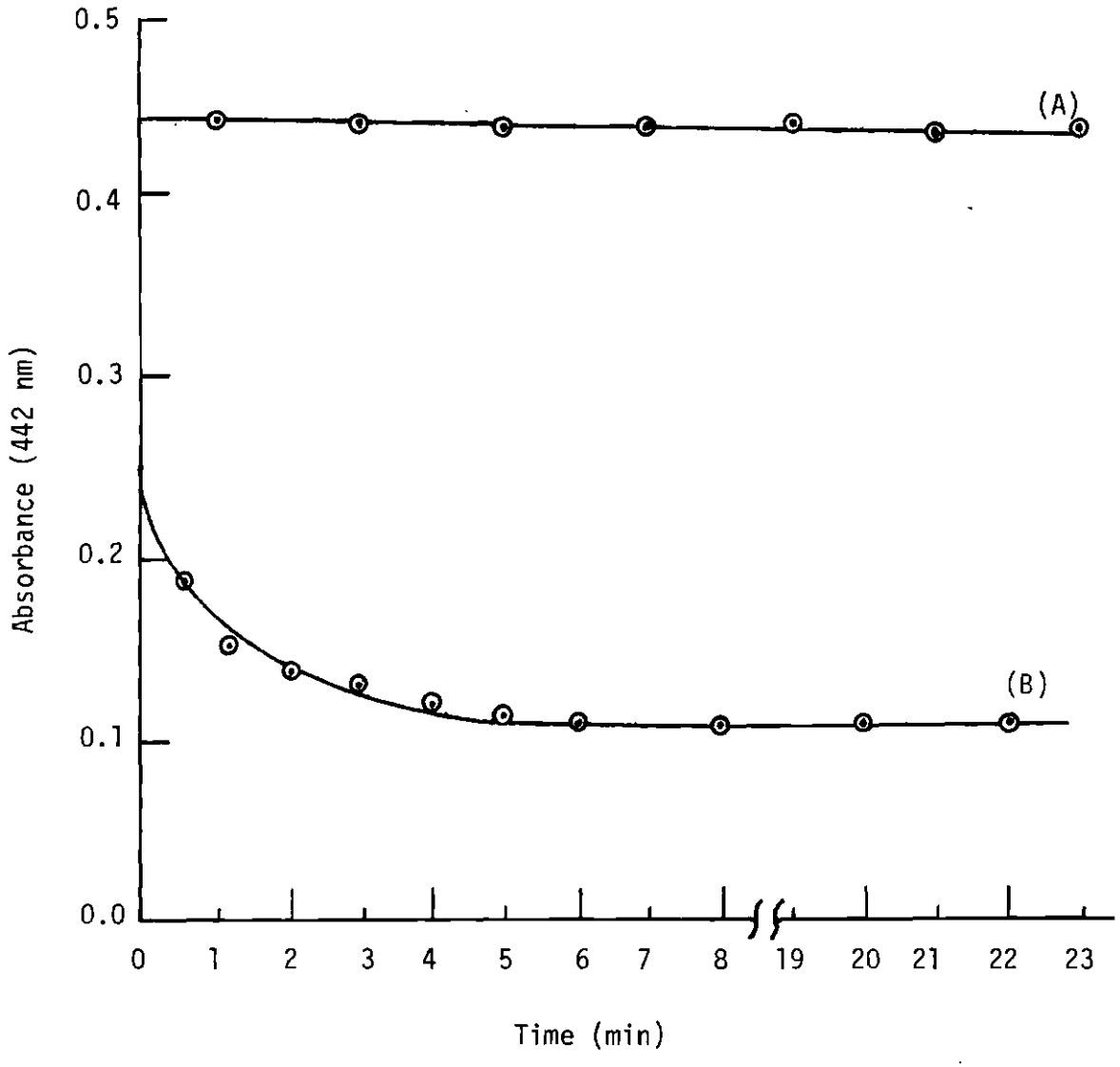


Figure 7. Results of Addition of Ca-EDTA to Solutions of Ni-Murexide (A) and Copper-Murexide (B) in Aqueous Ammonia. The absorbance at 442 nm was monitored with the Phototitrator used for the nickel determination.

any laboratory. It offers a simple, straightforward method both for routine analysis of high purity cobalt, and for calibration of standards used for other techniques.

If the method has a drawback, it would be the sensitivity of the nickel-murexide complex to high ionic strengths. However this phenomenon has been shown to be far less serious than first believed, since salts are neither necessary for buffering the solution nor for masking of foreign ions.

CHAPTER IV

SOME OBSERVATIONS CONCERNING IONIC STRENGTH EFFECTS ON THE NICKEL-MUREXIDE COMPLEX AND THE QUALITY OF MUREXIDE END POINTS

Introduction

In Chapter III the development of a photometric EDTA titration of nickel in presence of large amounts of cobalt has been discussed. Cobalt is masked as the pentammine complex of cobalt(III), which is developed in concentrated aqueous ammonia. The ammoniacal solution is then diluted and nickel is titrated using murexide as the indicator. During the initial stages of development of this method, difficulties in obtaining a sharp end point break were sometimes encountered. In several cases the yellow nickel-murexide complex did not form at all. In these preliminary investigations ammonium chloride was added to the ammoniacal solution for the purpose of establishing a buffer; and it was observed that the distinctiveness of the yellow color, and hence the sharpness of the end point break, depended upon the amount of ammonium chloride added. As larger amounts of salt were added, there was an apparent decrease in purity of the yellow color, and the end point became less sharp. Initially it was thought that a pH effect was responsible for the observed phenomenon, but simple experiments showed this belief to be incorrect. Regardless of the amount of ammonium chloride added, the pH of the solution never moved outside the range within which the yellow color of the nickel-murexide complex persists. The yellow color also was observed to form

in solutions containing a wide range of ammonia concentrations from very dilute to very concentrated (15 F). If, however, increasing amounts of ammonium chloride were added to these ammoniacal solutions already containing the nickel-murexide complex, the original yellow solution acquired first a reddish hue, then the red became progressively more intense until the color appeared to the eye to be the violet of free murexide. It was then surmised that this phenomenon was caused by the increasing ionic strength in the solution. This idea could be proven by adding inert salts to an ammoniacal solution of the nickel-murexide complex. It should be noted that inert salts in this connotation are salts that contain neither a cation capable of complexing with murexide nor an anion capable of forming a complex with nickel. Several salts were investigated and are elaborated upon in the following discussion.

Experimental

Such inert salts as the chlorides, sulfates, and nitrates of sodium and potassium were investigated, and all of these showed the same effect on the nickel-murexide system as ammonium chloride.

For a more complete assessment of the observations, absorbance curves were taken of ammoniacal solutions containing nickel-murexide and varying concentrations of salts. In addition, absorbance curves were taken of similar solutions containing sucrose in order to get a comparison of results between electrolytes and nonelectrolytes. As expected, sucrose did not destroy or prevent the formation of the nickel-murexide complex.

The solutions were prepared according to the following procedure.

One milliliter of 10^{-2} F Ni^{2+} and 10.0 ml of concentrated aqueous ammonia were pipetted into each of a series of 100-ml volumetric flasks. For each substance investigated seven flasks were employed. Enough salt was added to these flasks to provide a concentration from 0.1 F to 1.5 F. When the salt was completely dissolved, 1.5 ml of a saturated solution of murexide was added, the solution was diluted to the mark, and the absorbance curve was recorded.

As the concentration of the salt increased, the absorbance at the nickel-murexide maximum of 442 nm decreased. As expected the absorbance at the free murexide maximum of 540 nm increased. With sucrose hardly any change in absorbance occurred even in solutions which were 1.5 F in the sugar. All 1:1 electrolytes produced the same results within experimental error. Only sodium sulfate was investigated as an example of a 1:2 electrolyte. As expected, at equimolar concentrations sodium sulfate had a greater effect on nickel-murexide than the other salts.

The results of the experiments are summarized in Tables 3 and 4 showing the absorbance values at the two peak maxima of 442 nm and 540 nm for solutions of various concentrations of the substances investigated. An even better comparison of the effect of the various substances can be obtained from the graphical representation in Figure 8. The curves in Figure 8 show quite dramatically the similar effect of all 1:1 electrolytes and the greater effect of sodium sulfate.

Discussion of Results

The data presented here were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer using a 1-cm cell. In order to obtain ab-

Table 3. Absorbance at 442 nm for Nickel-Murexide as a Function of Various Concentrations of Additives

Additive	Formality							
	0.0	0.1	0.2	0.3	0.5	0.8	1.0	1.5
NaCl	0.85	0.77	0.71	0.65	0.55	0.43	0.36	0.21
$NaNO_3$	0.85	0.78	0.72	0.67	0.57	0.47	0.38	0.30
KCl	0.82	0.76	0.72	0.66	0.57	0.47	0.41	0.30
KNO_3	0.80	0.75	0.70	0.65	0.60	0.52	0.47	0.35
Na_2SO_4	0.81	0.67	0.54	0.45	0.34	0.22	0.18	0.14
Sucrose	0.80	0.80	0.79	0.78	0.79	0.76	0.76	0.75

Table 4. Absorbance at 540 nm for Nickel-Murexide as a Function of Various Concentrations of Additives

Additive	Formality							
	0.0	0.1	0.2	0.3	0.5	0.8	1.0	1.5
NaCl	0.15	0.19	0.22	0.25	0.31	0.38	0.42	0.48
$NaNO_3$	0.16	0.19	0.22	0.25	0.30	0.35	0.40	0.45
KCl	0.16	0.20	0.22	0.25	0.29	0.34	0.37	0.44
KNO_3	0.14	0.16	0.18	0.20	0.25	0.29	0.30	0.35
Na_2SO_4	0.17	0.26	0.30	0.35	0.40	0.42	0.48	0.48
Sucrose	0.16	0.17	0.17	0.19	0.20	0.20	0.20	0.20

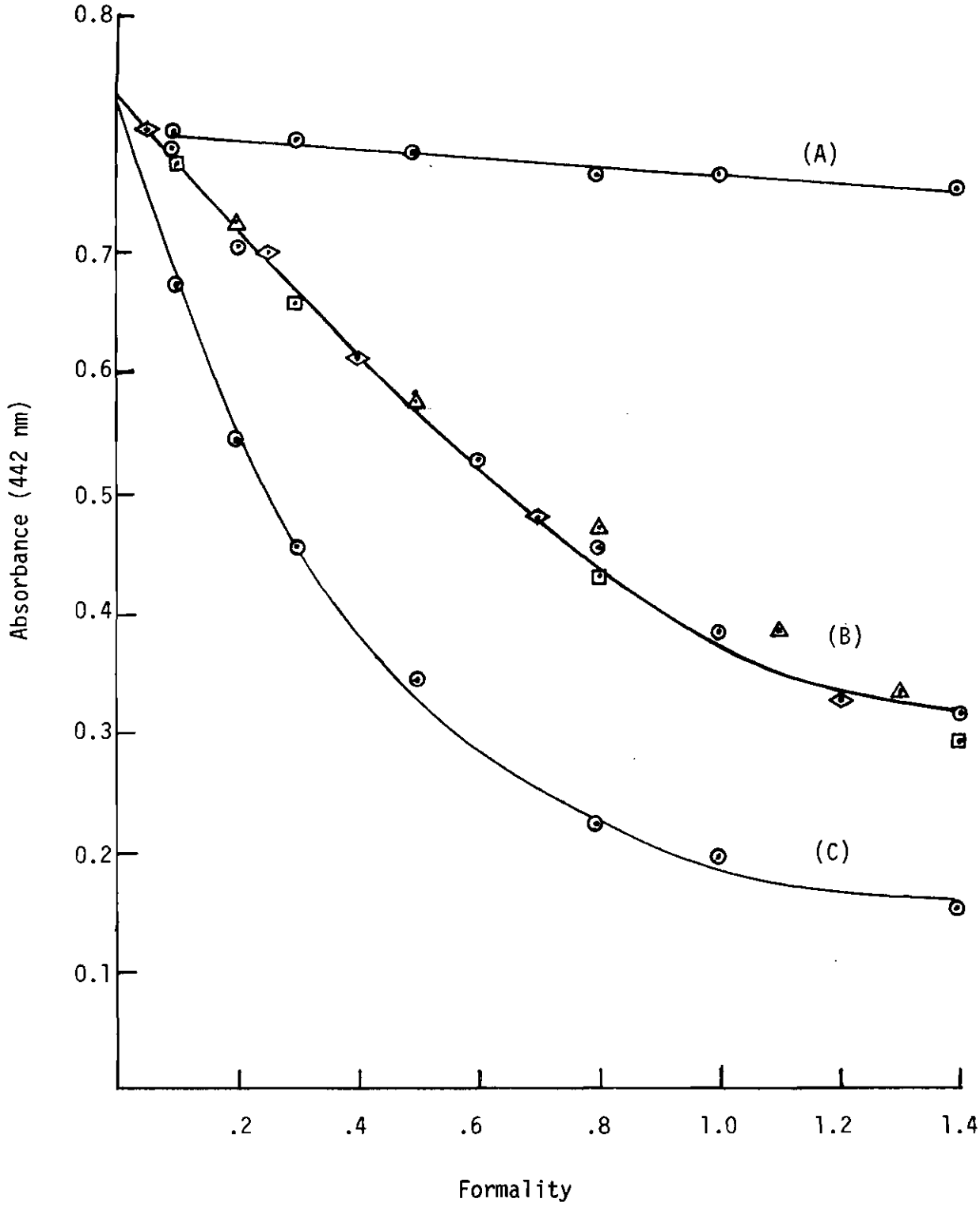


Figure 8. Effects of Various Additives on the Absorbance of Nickel-Murexide at 442 nm. (A) sucrose; (B) $NaNO_3$ (⊙), NaCl (⊡), KNO_3(◈), KCl (▲); C Na_2SO_4.

sorbance values large enough to permit accurate assessment of a change between solutions containing different amounts of salt, larger concentrations of nickel and murexide were used than were actually encountered in samples analyzed by the procedure in Chapter III. In these samples containing less nickel considerably lower concentrations of salts were needed to lower the degree of formation of nickel-murexide to an impractical level. The data in Tables 3 and 4 and the curves in Figure 8 show conclusively that the degree of formation of the nickel-murexide complex is dependent upon the ionic strength of the solution.

Complaints have been expressed by several workers concerning the low quality of murexide end points in some systems, especially with the cobalt-murexide system. It is quite likely that an ionic strength effect was responsible for the low quality of the color change at the end points, since further qualitative studies showed that the behavior described herein is not unique to nickel. In fact the effect appears to be even more pronounced with the cobalt-murexide complex.

The procedure for titrating cobalt using murexide indicator is as follows. Murexide is added to the weakly acidic solution containing the cobalt ion. A red-orange color forms, and NH_3-NH_4Cl pH 10 buffer is added dropwise until the color changes to pure yellow (16,17). The solution is then diluted and titrated with EDTA. It has always been advised that excessive amounts of buffer are to be avoided. The opinion has been advanced that too high an ammonia concentration causes the formation of the ammine complexes with destruction of the cobalt-murexide complex. However it has been observed in the investigations reported here that if murexide is added to concentrated (15 F) aqueous ammonia containing some

cobalt ions, the yellow cobalt-murexide complex does form. However, the color is readily discharged by addition of the inert salt. It was also observed that at very large concentrations of ammonia somewhat less salt was required to destroy the yellow color. Such behavior was to be expected because of the added effect of strong complexation by ammonia.

In the light of this investigation it is recommended that when difficulties are encountered with metal murexide systems, ionic strength effects should be suspected as a possible cause. In many cases simply diluting the solutions may solve the problems.

CHAPTER V

THE USE OF PAN FOR AN EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF NICKEL IN PRESENCE OF COBALT

Introduction

A photometric titration of small amounts of nickel in presence of cobalt has been developed and is described in Chapter III. In this method cobalt was masked as the pentammine complex of cobalt(III), and nickel was titrated with EDTA using murexide as the indicator. The method is applicable to analysis of samples containing nickel at molar ratios to cobalt of approximately 1:10,000. As discussed in Chapter III, the method is limited to these ratios because of the lack of an adequate phototitrator light source and not the inability to mask greater amounts of cobalt.

In this method the masking of cobalt was quite effective. Therefore it was decided that if a suitable chromogenic agent could be found, a photometric determination in combination with an extraction technique would circumvent the problem of the high color background due to the cobalt, which was ultimately the limiting factor in the photometric titration.

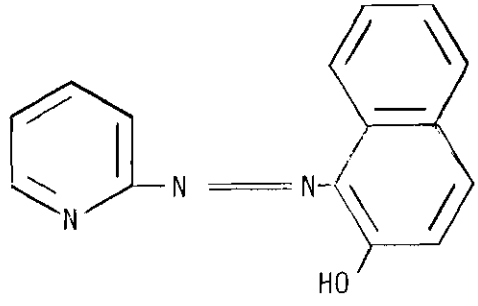
At the time that the idea for an extraction method was being conceived, work on some other systems was being carried out in our laboratory using 1-(2-pyridylazo)-2-naphthol (PAN) as the chromogenic agent (18,19). A brief investigation showed PAN to be a promising reagent for the determination of nickel in cobalt. A few remarks should be made at

this point concerning PAN and its uses.

PAN as a Chromogenic Agent

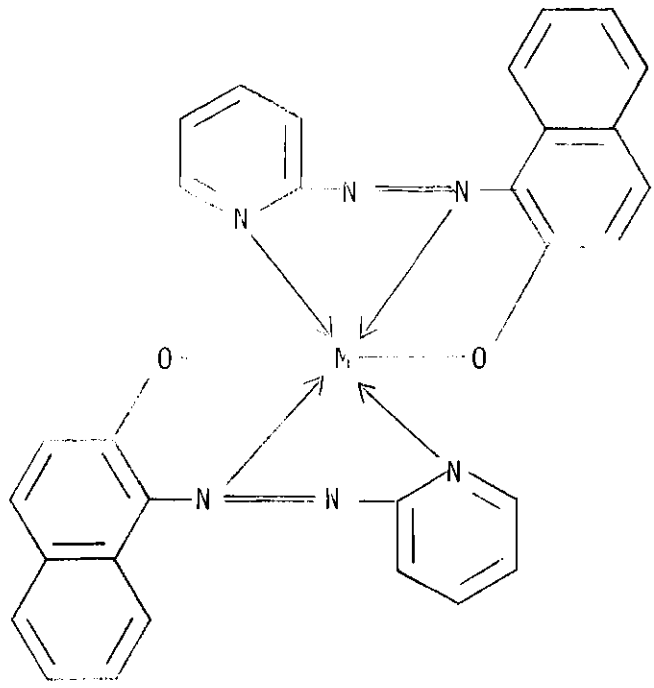
PAN was introduced in 1955 by Cheng and Bray (20) as a sensitive chromogenic reagent for metals and as an indicator in chelometric titrations; and since then it has been used in the determination of over thirty elements. The conditions for reaction of PAN with some metals, including nickel, have been studied by Püschel (21). The reagent has been used by Püschel and coworkers (22) to determine microgram quantities of nickel, cobalt, and iron in the same sample, when present in comparable amounts. Nakagawa and Wada (23) have also used PAN for the determination of nickel in the presence of cobalt with both metals present at the microgram level.

PAN is a red-orange solid practically insoluble in water, but soluble in a variety of organic solvents. Nakagawa and coworkers (24) have reported a value of $10^{5.1}$ for the distribution coefficient for PAN in a chloroform-water system. The structural formula of PAN is the following:



Shibata (25) has identified three forms of PAN, (1) a protonated form which is soluble in aqueous acidic solution, (2) a yellow neutral form, which is insoluble in water, and (3) an ionic form present in basic solution. PAN is extracted into chloroform from both acidic and basic media. The absorbance curves of such extracts are shown in Figure 9.

PAN forms intensely colored complexes with many metals. The majority of the complexes show a metal to PAN ratio of 1:2, when formed in presence of excess PAN and have the following structural formula:



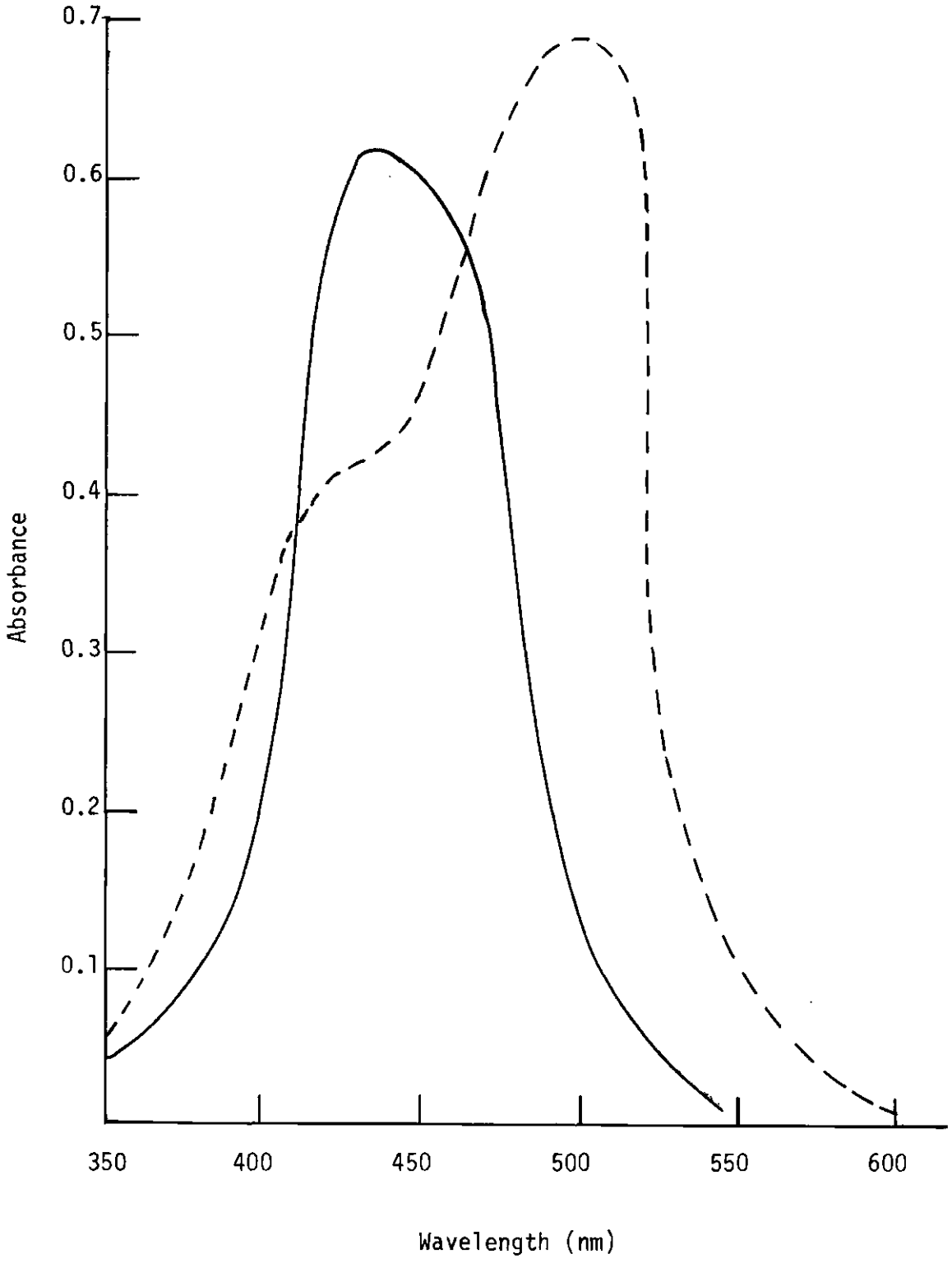


Figure 9. Spectral Curves of PAN in 30:70 Ethanol:Chloroform
Acidic _____, Basic ------.

The colors of these panates* are various shades of red except that of vanadium(V) which is deep purple, and palladium(II) and cobalt(III) which are green. The complexes are generally soluble in water but are readily extracted into various organic solvents. The conditions for these extractions have been studied by Püschel (21) and Shibata (27).

The current status of PAN and its use in the determination of numerous metals including nickel, is dealt with in a review by Shibata (25).

Preliminary Investigations

Systematic investigations were begun on the chloroform extraction of nickel panate from solutions containing nickel both alone and in presence of cobalt(III) pentammine. Since both free PAN and the nickel panate are insoluble in water, initial investigations were performed on 1:2 alcohol-water solutions. To solutions containing nickel, excess PAN was added. The nickel panate which formed was extracted with several small volumes of chloroform. Enough ethanol was added to the extract to make a 30:70 alcohol-chloroform solution in order to solubilize any water inadvertently carried over into the extract. The water:ethanol:chloroform phase diagram has been reported (19). Figure 10 shows the absorbance curve of the red nickel panate extracted into chloroform from slightly ammoniacal solution. For purpose of reference the cobalt(III) panate curve is also shown.

The extraction of nickel panate as a function of pH was studied. Several solutions, all containing 5.0 ml of 3.6×10^{-5} F nickel nitrate

*Nomenclature suggested by W. Berger and U. H. Elvers (26).

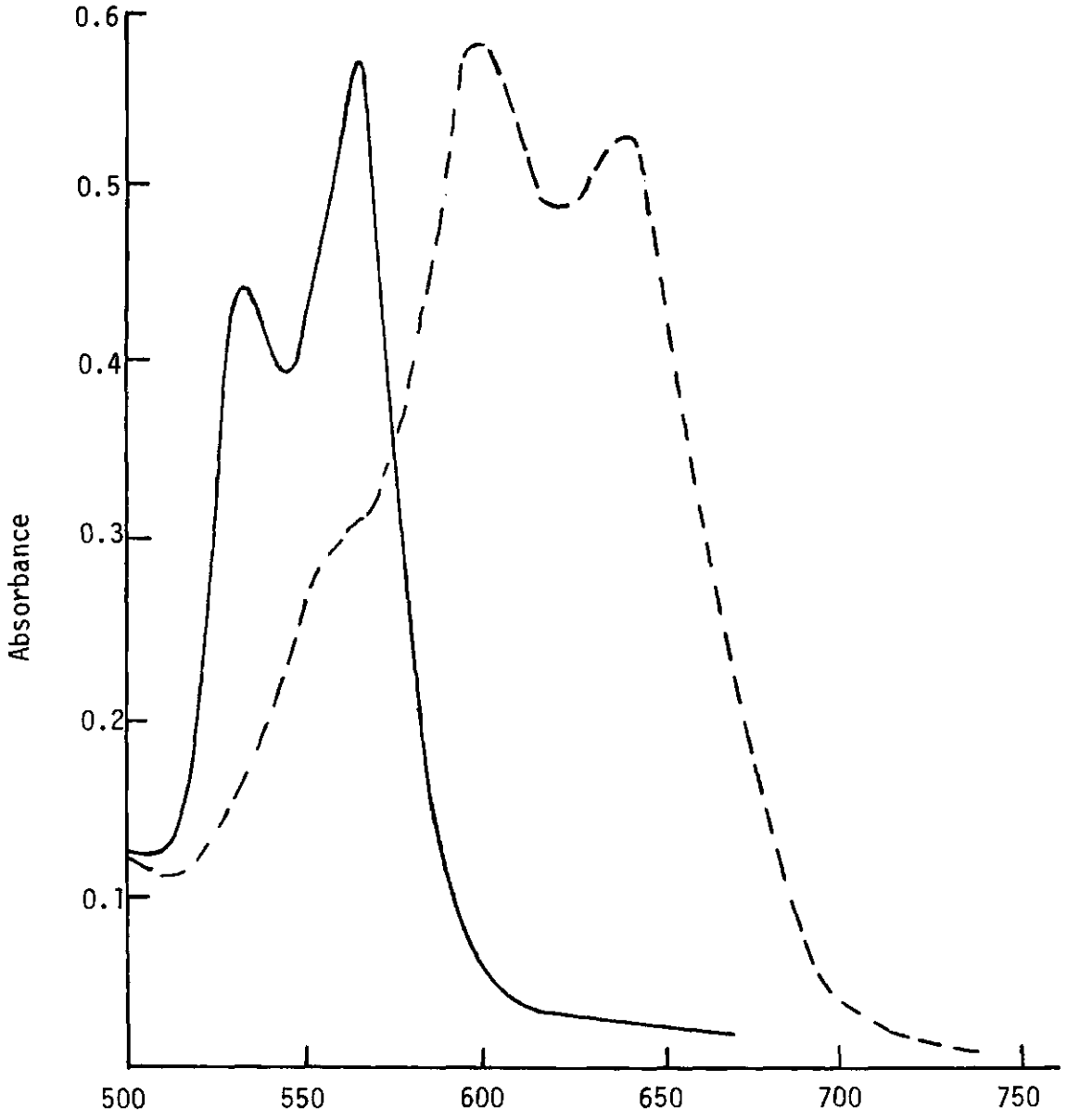


Figure 10. Spectral Curves of Metal Complexes of PAN in 30:70 Ethanol Chloroform. Nickel(II)_____, Cobalt(III)------.

in about 50 ml of water were prepared. The various solutions were adjusted to pH values between 3.5 and 10.0 by dropwise addition of dilute hydrochloric acid and dilute aqueous ammonia as required. PAN as added and the solutions were shaken for thirty seconds and then allowed to stand for several minutes. The nickel panate was then extracted with three 8-ml portions of chloroform. The extracts were made ethanolic and diluted to 50.0 ml, and their absorbance, with reference to a reagent blank, was taken at 568 nm. Figure 11 shows that recovery of nickel as the panate in the chloroform extraction is complete between "pH" 5 and "pH" 9.2.* Similar results for benzene extracts of nickel panate from methanolic solutions have been reported by Shibata (27). Püschel reported the same results for a chloroform extract from methanolic solutions (21).

It was observed that the reaction between nickel and PAN was considerably slower in acidic than in basic media. In order to obtain complete complex formation in acid media, either longer standing or warming is required. Once conditions were established for complete extraction of nickel panate, attention was directed to the investigation of solutions containing cobalt.

Solutions of the cobalt(III) pentammine complex were prepared according to the procedure outlined in Chapter III. The solutions were made alcoholic and then were adjusted to approximately "pH" 8.5 with a suitable acid. PAN was added and after a few minutes of standing the extraction with chloroform was effected and the absorbance curves of the

*The author is aware that in such an alcoholic solution this is not a true pH value. However the term "pH" is used for convenience.

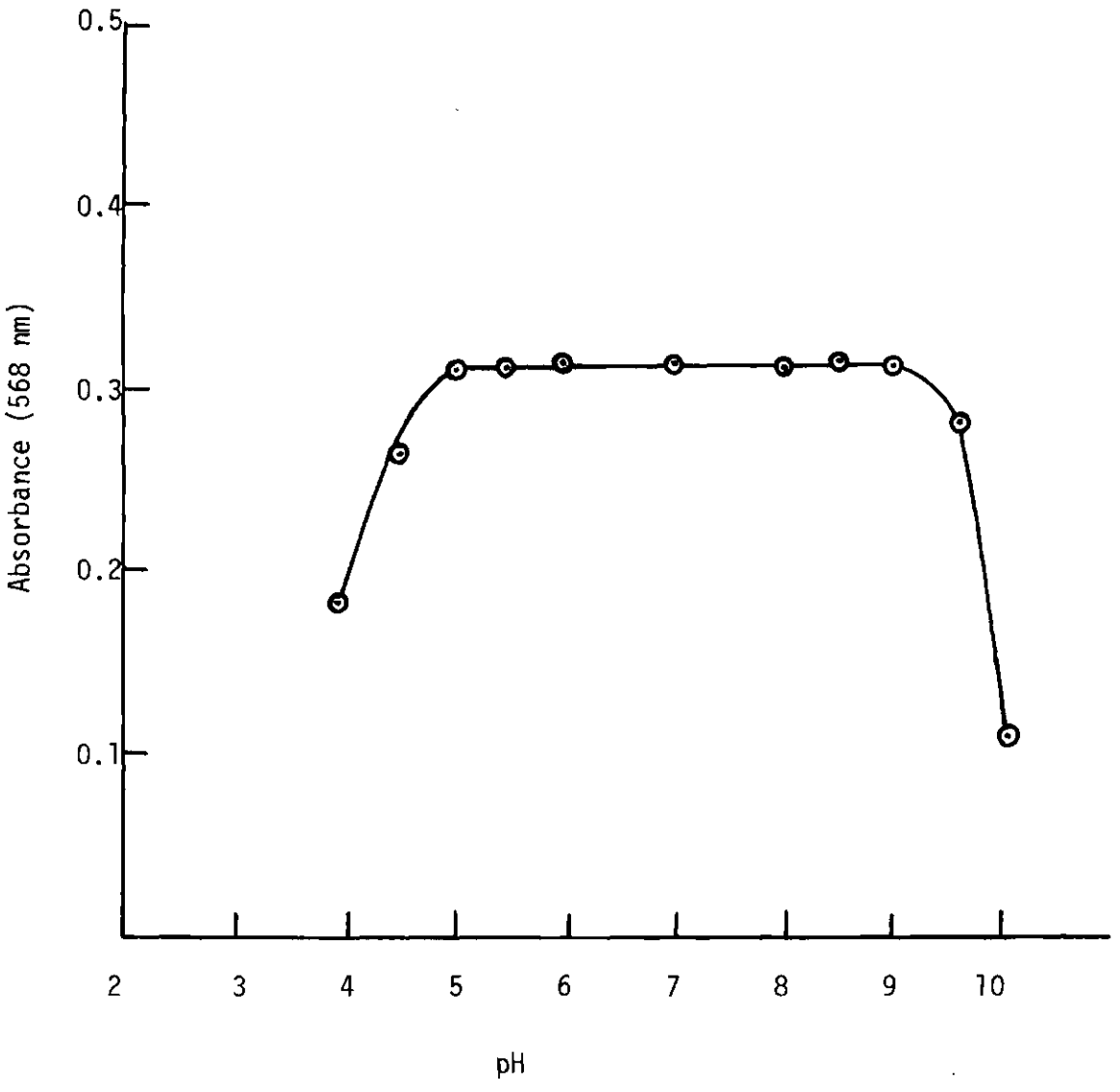


Figure 11. Effect of pH on the Extraction of Nickel-PAN Into Chloroform. (14.7 µg Ni Extracted as the Panate into 50 ml Chloroform.)

extracts were taken. The curves showed that all extracts contained green cobalt(III) panate.

In these investigations the solutions of cobalt(III) pentammine differed from those in the titration procedure of Chapter III in pH; and furthermore, alcohol was present. Both of these factors were studied to determine their influence on the formation of the cobalt(III) panate. It was discovered that alcohol in any concentration promoted formation of the green panate. However, when solutions containing the cobalt(III) pentammine complex, but no alcohol, were adjusted to pH 8.5, treated with PAN, and subjected to a chloroform extraction, no cobalt panate was found in the extract.

The adjustment of the pH was found to be a critical but controllable factor. It is necessary to add the acid dropwise and with vigorous stirring to prevent the formation of spots of high acidity at which apparently some cobalt(III) pentammine is decomposed thus making the cobalt available for reaction with PAN.

Next, studies were made to determine what effects, if any, the absence of alcohol had on the formation and extraction of the nickel panate. Solutions containing no alcohol but the same amount of nickel as those investigated previously, were prepared. The pH was adjusted as before and PAN was added. As expected, the rate of formation of nickel panate was considerably lower than in alcoholic solutions. However, if the solutions were allowed to stand for a few minutes before being extracted with chloroform, complete recovery of nickel was accomplished. The curve in Figure 11 was exactly reproduced.

Next, some cobalt was added to several solutions containing the same amounts of nickel as those above. The solutions were treated according to the established procedure for masking cobalt as the pentammine complex. The pH value of a series of solutions were adjusted between 5 and 9 by careful, dropwise addition of 1:1 sulfuric acid, and PAN was added. The solutions were allowed to stand for several minutes and then extracted with chloroform. Extracts from solutions with pH greater than about 7.5 gave correct results, but from solutions of pH less than 7.5 the results were slightly high. Spectral curves on the extracts which gave high results indicated the presence of cobalt(III) panate. Therefore low pH values had to be avoided.

At this point a workable procedure could be developed. Figure 12 shows schematically the major steps involved.

Development of the Analytical Method

Several aspects of the procedure outlined in Figure 12 were studied in detail to achieve optimum conditions for determination of nickel. Careful investigations showed that after addition of PAN to the solutions of nickel, a standing time of three and one half minutes were required for complete formation of nickel panate. Times of standing up to ten minutes were studied and were observed not to be detrimental.

The color stability of the nickel panate was also studied. No change in the absorbance for at least twenty-four hours was observed on a solution containing the complex in 30:70 alcohol-chloroform. Longer times were not investigated. A study was also conducted to establish the effect of solvent composition of the absorptivity of the nickel panate.

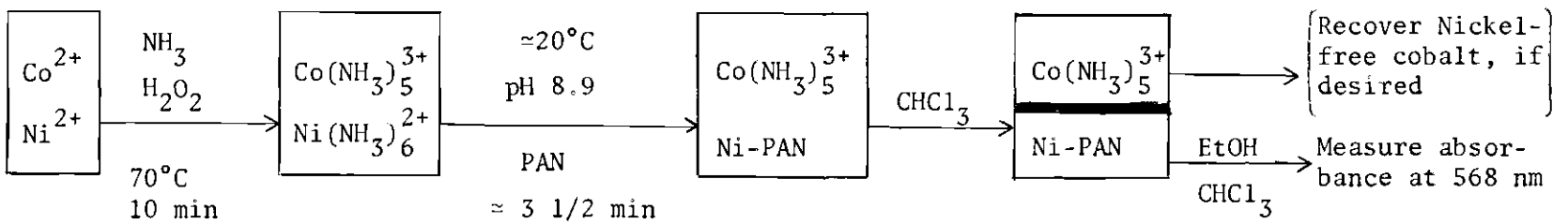


Figure 12. Schematic Diagram of the Procedure for the Determination of Nickel in Cobalt.

Two solutions containing identical concentrations of nickel panate, one in chloroform and one in ethanol, were prepared. The absorbance values of the two solutions at 568 nm were the same within experimental error. When these solutions were mixed in various proportions and the absorbance of the mixtures measured at 568 nm, no significant variation of the absorbance with changes in the solvent composition was discernible.

Next, solutions containing cobalt were investigated. The reaction for forming the pentammine complex of cobalt(III) had been well characterized in the description of the titration method (Chapter III). However in the method outlined in Figure 12 for the spectrophotometric determination of nickel, it is necessary to acidify the solution to lower the pH to 8.9. Preliminary investigations here revealed that extreme care should be exercised in adjusting the pH; otherwise some cobalt(III) pentammine is decomposed causing formation of an interfering cobalt panate. Further investigations were conducted here to establish the optimum conditions and technique for treating the solution. A 1:1 sulfuric acid solution was found to be most suitable for adjusting the pH. Nitric acid is also suitable. Hydrochloric acid is undesirable primarily because of the volatility of both hydrogen chloride and ammonia. Much ammonium chloride "smoke" is formed which is obnoxious and can be detrimental to the pH meter. Phosphoric acid cannot be used due to precipitation of phosphates of both cobalt and nickel.

The temperature of the solution increases considerably during the addition of acid. Therefore it is recommended to place the vessel containing the solution in an ice bath and reduce the temperature to about 10°C. The solution is then vigorously stirred and acid is added drop-

wise. When the adjustment of pH is complete, the solution should be very near to room temperature. A final pH of 8.9 was established which was found to be optimum.

During these investigations it was discovered that the large amounts of reagents used, namely aqueous ammonia and sulfuric acid, introduced impurities which gave a rather high blank value. These impurities were not identified but it was found that they could be effectively masked by addition of tiron; thereby the blank was reduced to a level which seems to be entirely due to the absorbance of free PAN at the operating wavelength. Later investigations showed tiron to be effective in masking a large number of ions. A detailed discussion is deferred to a later section of this chapter.

As a final step in this development, studies were made to evaluate the sensitivity of the method. Investigations showed that the lower limit on the determination of nickel was fixed by the minimum quantity of nickel which could be quantitatively extracted from the aqueous solution. This quantity was found to be 0.04 μg/ml.

Procedure

1. Dissolve, in a 250-ml beaker, an amount of sample containing between 2 and 50 μg of nickel (Note a).

2. Add to the solution concentrated aqueous ammonia, with vigorous stirring, until all of the initial precipitate has redissolved. Then add 8 ml ammonia in excess.

3. Measure a total volume of 30% hydrogen peroxide such that at least 0.025 ml is taken for each milligram cobalt present. Of this volume, add one half to the solution from step (2). Cover the beaker with

a watch glass and place it in a water bath kept at 70 ±5°C for six minutes (Note b).

4. Wash down the watch glass and the sides of the beaker with a small amount of water from a wash bottle (Note c). Add the second portion of 30% hydrogen peroxide and leave in the water bath for four additional minutes.

5. Remove the solution from the water bath and allow it to stand until room temperature is reached (Note d).

6. Place the solution in an ice bath and allow the temperature to be lowered to approximately 10°C.

7. Remove the vessel from the ice bath, insert the electrodes of a pH meter, and add 1:1 sulfuric acid, dropwise and with vigorous stirring, to adjust the pH to 8.9 (Note e). Transfer the solution quantitatively to a separatory funnel of appropriate size (Note f).

8. Add 0.8 ml of 0.01 F PAN, shake for 10 seconds, and allow three and one half minutes standing time.

9. Extract the sample solution with three 8-ml portions of chloroform and combine the extracts in a 50-ml volumetric flask.

10. Add 15 ml of 95% ethanol and dilute to the mark with chloroform.

11. Measure the absorbance of the solution at 568 nm against a blank (Note g). Evaluate the result using a calibration curve.

Notes

a. Dissolve cobalt metal in a minimum amount of warm 1:1 nitric acid or warm concentrated (12 F) hydrochloric acid. Dissolve salts or other compounds as is appropriate.

b. Inconsistently high results were obtained if the temperature was allowed to go to 80°C even for a short period of time.

c. During the oxidation process the solution effervesces vigorously, and considerable spattering occurs. The spattered droplets must be washed back into the oxidizing medium. It is desirable that the total solution volume after final addition of hydrogen peroxide be no greater than about 60 ml.

d. A standing time of one and one half to two hours is usually sufficient.

e. Add tiron, potassium iodide, and tartrate to mask foreign ions at this point.

f. The total solution volume at this point should not be greater than 100 ml. Use only separatory funnels with teflon stopcocks.

g. Obtain data for a calibration curve from cobalt-free solutions containing from 2 to 50 µg of nickel. It is of utmost importance that all masking agents added to the samples be added when preparing the blank and the standards for the calibration curve.

Discussion

Results

A typical calibration curve is presented in Figure 13. The molar absorptivity of the nickel panate in chloroform calculated from the slope of this curve is 5.22×10^4 liter/mole-cm. This value compares to 5.30×10^4 liter/mole-cm reported by Püschel and coworkers (22).* The Sandell sensitivity (28) is 1.1×10^{-3} µg/cm^2.

*Note that the absorbance values for the calibration curve were determined in a cylindrical cell with an effective pathlength of 11.7 mm.

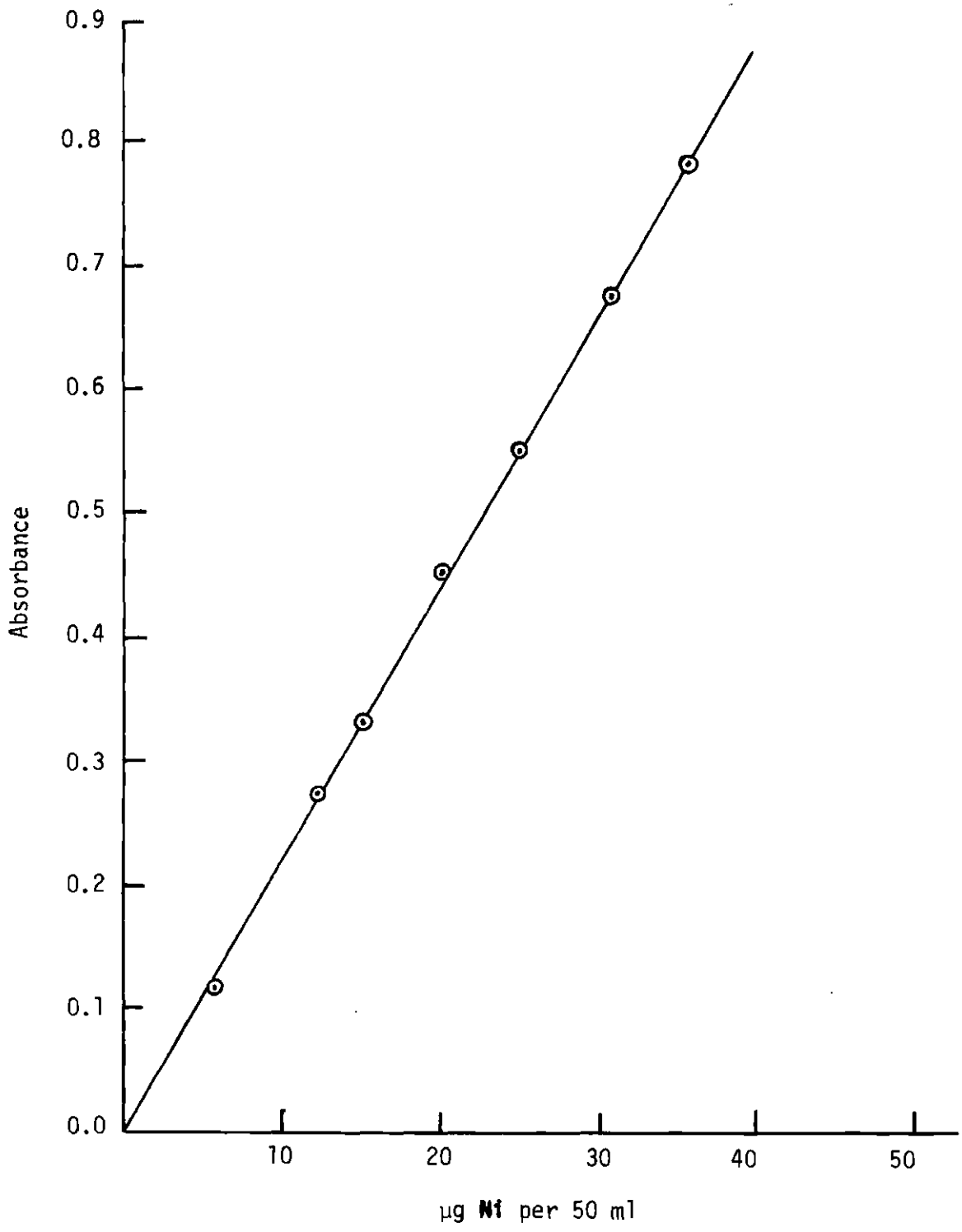


Figure 13. Nickel Calibration Curve

Table 5 presents the results obtained for the determination of nickel when present alone. The data show good accuracy and precision.

The influence of cobalt on the determination of nickel was assessed by addition of cobalt to solutions containing known amounts of nickel and then analyzing for the latter metal. For levels of nickel up to approximately 0.002 per cent, the K&K Laboratories cobalt described in Chapter II was used. At lower nickel levels high results were obtained using this cobalt and corrections had to be applied. For extreme cobalt:nickel ratios the correction factor became prohibitively large. Furthermore it was impossible to prepare synthetic samples of higher cobalt:nickel ratios than that of the cobalt at hand, which ratios were far above the sensitivity of the method.

Therefore, it became necessary to prepare "nickel-free" cobalt. Such cobalt was obtained by the procedures described in Chapter VI, and was used directly in the preparation of synthetic samples of very low nickel content. The synthetic samples were analyzed for nickel and the results are shown in Table 6. The lower limit of nickel that can be determined by this method is approximately 0.0005 per cent relative to cobalt. There are two factors which fix this limit. First, as mentioned previously, the lower level of nickel that can be completely extracted from an aqueous solution is about 0.04 μg/ml. Second, under the conditions of the procedure the upper limit of the quantity of cobalt that can be effectively masked is 0.96 g. Solutions containing greater amounts of cobalt gave high results for nickel, and further investigation showed that some cobalt(III) panate was formed.

Table 5. Results of Spectrophotometric Determination of Nickel when Present Alone

µg Nickel			
Taken	Found	Difference	% Difference
2.1	2.3	+0.2	9.5
2.1	2.1	0.0	0.0
4.2	4.1	-0.1	2.4
6.3	6.3	0.0	0.0
6.3	5.9	-0.4	6.3
6.3	6.3	0.0	0.0
8.4	8.3	-0.1	1.2
8.4	8.5	+0.1	1.2
10.5	10.7	+0.2	1.9
10.5	10.2	-0.3	2.8
10.5	10.5	0.0	0.0
12.6	12.4	-0.2	1.6
12.6	12.8	+0.2	1.6
14.7	14.7	0.0	0.0
14.7	14.8	+0.1	0.7
16.8	17.6	+0.8	4.8
21.0	21.0	0.0	0.0
21.0	21.3	+0.3	1.4
25.2	25.2	0.0	0.0
25.2	24.5	-0.7	2.8
31.5	31.9	+0.4	1.3
38.8	40.3	+0.5	1.3
38.8	41.7	+0.7	1.8
42.0	41.7	-0.3	7.1
52.5	52.1	-0.4	0.8
52.5	53.4	-0.9	1.7

Table 6. Results of Spectrophotometric Determination of Nickel in Presence of Cobalt

μg Nickel				Co:Ni Molar
Taken	Found	Difference	% Difference	Ratio
42.0	41.7	-0.3	0.7	160
42.0	41.8	-0.2	0.5	160
21.0	20.6	-0.4	1.9	315
21.0	21.1	+0.1	0.5	315
10.5	10.8	+0.3	2.8	630
10.5	10.5	0.0	0.0	630
42.0	42.2	+0.2	0.5	800
42.0	42.5	+0.5	1.2	800
4.2	3.5	-0.5	11.9	1600
4.2	3.9	-0.3	7.1	1600
10.5	10.2	-0.3	2.8	3150
10.5	10.3	-0.2	1.9	6300
10.5	10.9	+0.4	3.8	6300
10.5	10.5	0.0	0.0	6300
6.3	6.3	0.0	0.0	10,500
6.3	5.9	-0.4	6.3	10,500
5.3	5.3	0.0	0.0	20,500
5.3	5.8	+0.5	9.4	20,500
10.5	10.9	+0.4	3.8	44,500
10.5	10.3	-0.2	1.9	44,500

Table 6. Results of Spectrophotometric Determination of Nickel in Presence of Cobalt (Concluded)

µg Nickel				Co:Ni Molar Ratio
Taken	Found	Difference	% Difference	
8.4	8.6	+0.2	2.4	55,600
8.4	8.1	-0.3	3.6	55,600
10.5	10.2	-0.3	2.8	66,700
10.5	11.1	+0.6	5.7	66,700
8.4	9.2	+0.8	9.5	83,400
6.3	7.0	+0.7	11.1	111,200
6.3	5.9	-0.4	6.3	111,200
5.3	5.0	-0.3	5.7	137,000
5.3	4.6	-0.7	13.2	137,000
5.3	5.8	+0.5	9.4	181,000
5.3	6.2	+0.9	17.0	181,000
4.2	5.3	+1.1	26.0	224,000
4.2	5.1	+0.9	21.4	224,000

Interferences

The pH at which the method here described is carried out is in the region where many metal ions react with PAN. In addition many metals precipitate as hydroxides, and thus, present a potential interference. Therefore studies were necessary to develop means of eliminating these interferences. Masking is the most desirable approach, and the interference of most commonly occurring elements was obviated by this technique. The results of extensive work on investigation of foreign ions and their potential to interfere are summarized below. No attempt was made to determine tolerance limits of most of the elements studied, but in all cases the level of these elements is far greater than their expected level in high purity cobalt.

Several elements have not been reported or observed to form panates. These include the alkali metals, the alkaline earth metals, Cr, Tc, Re, and the actinides (excluding Th and U) (22). Therefore these elements do not directly interfere with the determination of nickel and in general are of little concern. However, indirect interferences are possible by adsorption or occlusion if a substance forms a precipitate. This type of interference is demonstrated by barium and strontium which form sulfates in this method. They can, nevertheless, be tolerated in at least a twentyfold molar excess over nickel.

Specific masking techniques have been developed for most of the elements which do form panates under the conditions of this method. Table 7 presents results for determination of nickel in presence of many foreign ions, most of which are masked.

Of the masking agents used, tiron proved to be especially useful.

Table 7. Results of Spectrophotometric Determination of Nickel in Presence of Cobalt and Some Additional Foreign Metal Ions. (Enough Cobalt was present in each sample to provide a Cobalt:Nickel Ratio of 20,500.)

µg Nickel				Metal	M:Ni Mol-	Masking	Notes
Taken	Found	Difference	% Difference	Added	ar Ratio	Agent	(Below)
10.5	10.5	0.0	0.0	Fe	56	Tiron	a
21.0	21.5	+0.5	2.4	Fe	56	"	
10.5	10.9	+0.4	3.8	Fe	112	"	
10.5	10.8	+0.3	2.8	Cr	56	-----	b
10.5	10.2	-0.3	2.8	Cr	112	-----	
10.5	10.6	+0.1	1.0	Pb	56	Tiron or KI	
21.0	20.7	-0.3	1.4	Pb	70	"	
10.5	10.6	+0.1	1.0	Pb	112	"	
10.5	10.5	0.0	0.0	Pb	140	"	
10.5	10.5	0.0	0.0	Ag	112	NH_3 or KI	
10.5	10.2	-0.3	2.8	Ag	112	"	
10.5	10.6	+0.1	1.0	Al	112	Tiron	
10.5	10.9	+0.4	3.8	Al	140	"	
21.0	21.3	+0.3	1.4	Hg	56	KI	c
10.5	11.0	+0.5	4.8	Hg	112	"	c
10.5	11.0	+0.5	4.8	Bi	28	Tiron	
10.5	11.5	+1.0	9.5	Bi	56	"	d
10.5	12.1	+1.6	15.2	Bi	112	"	d
10.5	12.2	+1.7	16.2	Cu	3	-----	e
10.5	12.0	+1.5	14.2	Cu	3	-----	e
10.5	10.5	0.0	0.0	Cd	3	-----	f
10.5	11.2	+0.7	6.7	Cd	6	-----	f
10.5	10.2	-0.3	2.8	Mn	56	Tiron	
10.5	10.4	-0.1	1.0	Mn	112	"	
10.5	11.2	+0.7	6.7	Pd	10	"	
10.5	10.5	0.0	0.0	Pd	20	"	
10.5	9.7	-0.8	7.6	Sn(II)	56	-----	g
10.5	9.6	-0.9	8.6	Sn(IV)	56	-----	
10.5	11.5	+1.0	9.5	Sb(V)	56	Tiron	
10.5	10.0	-0.5	4.8	Ga	112	"	
10.5	10.4	-0.1	1.0	In	112	"	
10.5	9.7	-0.8	7.6	Rh	20	"	
10.5	10.3	-0.2	1.9	Ce(III)	112	"	
10.5	10.5	0.0	0.0	Ce(IV)	112	"	h

Table 7. Results of Spectrophotometric Determination of Nickel in Presence of Cobalt and Some Additional Foreign Metal Ions. (Enough Cobalt was present in each sample to provide a Cobalt:Nickel Ratio of 20,500.) (Concluded)

μg Nickel				Metal	M:Ni Molar Ratio	Masking Agent	Notes (Below)
Taken	Found	Difference	% Difference	Added			
10.5	10.6	+0.1	1.0	Th	112	Tiron or Tartrate	
10.5	10.9	+0.4	3.8	V(V)	56	Tiron or H_2O_2	
4.2	3.9	-0.3	7.1	U(V)	56	H_2O_2	
10.5	10.3	-0.2	1.9	Zn	3	-----	i
10.5	10.0	-0.5	4.8	Zn	6	-----	i

a. Unless otherwise noted one spatula tipfull of tiron, corresponding to about 0.2 g, was added.
b. Chromium(III) is oxidized to CrO_4^{2-} by H_2O_2.
c. One gram of KI was added.
d. Two spatula tips full of tiron was added.
e. The total extract was shaken with 2.0 F HCl for one and one half minutes. The aqueous phase was separated, brought to pH 5, KI and ascorbic acid were added to mask the Cu, and the solution was shaken for a few seconds. PAN was added and the nickel panate extracted per usual.
f. Total extract of cadmium and nickel panates were shaken with buffer pH 5. Cadmium panate was destroyed. Nickel was determined per usual.
g. Any tin(II) present initially in the sample is oxidized to tin(IV) by H_2O_2.
h. Cerium(IV) oxidizes tiron. However, if an excess of tiron is added, the Cerium(III) is masked.
i. Total extracts of nickel and zinc panates are shaken with 0.01 F HCl for six seconds.

It was first used to mask iron but was found to be quite effective with other metals including lead, aluminum, bismuth, manganese, palladium, antimony, gallium, indium, rhodium, cerium, thorium, and vanadium. Tiron is oxidized by cerium (IV), but if tiron is added in excess, the cerium(III) produced is effectively masked against reaction with PAN. Potassium iodide was used to mask mercury, as well as lead and large amounts of silver. Smaller amounts of silver were masked also by ammonia. Hydrogen peroxide, already established as a masking agent for vanadium(V) (29), was found to be effective at masking uranium(V).

Cadmium, zinc, and copper presented special problems in that no suitable masking reagents could be found for these metals. However techniques were developed to successfully handle these elements.

If cadmium is present in a sample, both the cadmium and nickel panates are extracted into chloroform. The total extract is then shaken for three or four seconds with acetic acid-acetate buffer pH 5. The cadmium panate is destroyed and cadmium returns to the aqueous phase while the nickel panate remains in the chloroform phase.

Zinc is also extracted as a panate along with nickel. When the extract is shaken with 0.01 F hydrochloric acid, the zinc returns to the aqueous phase, while the nickel panate remains in the chloroform. Solutions containing 10.5 μg of nickel and up to 71 μg of zinc, both as panates were shaken with 0.01 F hydrochloric acid. At least six seconds are required for complete removal of zinc. When the solutions are shaken for longer than fifteen seconds, some nickel is lost to the aqueous phase. Cadmium panate, of course, is also decomposed by this process, and the buffer pH 5 washing may be omitted if both zinc and cadmium panates are

to be destroyed. If, however, no zinc is present, it is more convenient to wash with buffer pH 5 since careful time control is not necessary.

To obviate the interference of copper is a more complex problem which was solved as follows. The chloroform solution of the panates of copper and nickel was shaken with 2 F hydrochloric acid whereby the two metals return to the aqueous phase. The chloroform was discarded and the aqueous phase containing nickel and copper was transferred to a 100-ml beaker. One gram of potassium iodide and a spatula tip full of ascorbic acid were added and the solution was adjusted to pH 5. A few milliliters of acetic acid-acetate buffer pH 5 were added and the solution was shaken for one minute. PAN was added and nickel panate was extracted according to the established procedure. Samples containing 10.5 µg copper were treated in this manner and the nickel was determined with an error of 14 per cent relative. Thiourea or thiosulfate can be substituted for potassium iodide and ascorbic acid, but no particular advantage is realized.

Tin, when present in a fiftyfold molar excess over nickel, caused low results for nickel. Only tin(IV) exists in these samples since any tin(III) is oxidized by hydrogen peroxide. Other workers (18,19) have reported similar low results caused by tin(IV) in zinc and cobalt panate extractions. As of this date the mechanism of the interference due to tin(IV) remains unresolved. A red tin panate has been reported to exist (25), but none was observed in this work. In any event this interference is of no consequence since high purity cobalt should not contain greater amounts of tin than can be tolerated by this method.

Conclusions

The method here developed has been demonstrated to be satisfactorily accurate and precise for determination of nickel in high purity cobalt. The method is applicable to determination of nickel at a level of 0.0005% relative to cobalt. By employing suitable masking agents, and by altering the basic procedure slightly in presence of copper, cadmium, or zinc, the method is virtually free of interferences. The method outlined here shows promise for application in three areas. First, the method provides a technique for the determination of low levels of nickel without need for expensive or complex instrumentation. Second, it offers a straightforward method for calibration of standards of other techniques of analysis. Third, the method is a suitable technique for analysis of nickel in cobalt samples of varying composition.

CHAPTER VI

FACILE METHODS FOR REDUCING THE NICKEL CONTENT OF COBALT SALTS

Introduction

During the development of the methods for determination of nickel in high purity cobalt and cobalt salts as described in Chapters III and V, it became apparent that a simple method for preparing large amounts of cobalt low in nickel and also some "nickel-free" cobalt was needed. Commercially available "reagent grade" cobalt salts contain from 0.15 to 1.0 per cent nickel relative to cobalt metal. Cobalt of various degrees of purity is available by custom order from a few sources, however, at very high cost. In addition the desired purity may be questionable.

The most commonly used method for preparing cobalt of low nickel content is that of Feigl (30). This method is based upon the precipitation of nickel as the dimethylglyoximate from a cyanide medium. It is useful for preparation of small amounts of "nickel-free" cobalt. However the method requires large quantitives of dimethylglyoxime and cyanide and, in addition, it is extremely time consuming. It is not a feasible method for preparing large amounts of "nickel-free" cobalt.

Controlled potential electrolysis is a feasible method for producing cobalt of low nickel content, but like the Feigl method, it is not practical for preparation of large amounts of cobalt.

Preparation of Cobalt of Low Nickel Content

The method here described is based upon the preparation of $Co(NH_3)_6Cl_3$ outlined by Bjerrum and McReynolds (14), and is suitable for preparation of very large amounts of cobalt salt of low nickel content.

Purification Procedure I

1. Dissolve, in a 2-liter beaker, 300 grams of cobalt nitrate hexahydrate (technical or better) and 160 grams of pure ammonium chloride in about 200 ml distilled water.

2. Add four grams of activated charcoal and 500 ml of concentrated aqueous ammonia.

3. Bubble air through the solution, by means of a large-bore bubbler, for four hours.

4. Filter off with a buchner funnel, the charcoal and the yellow salt formed and discard the filtrate.

5. Add the residue of charcoal and the salt to 1500 ml of water in a 3-liter beaker. Add 15 ml of concentrated hydrochloric acid to assure an acidic medium.

6. Heat on a hot plate until the salt is completely dissolved.

7. Filter through a buchner funnel to remove the charcoal.

8. Add to the filtrate concentrated hydrochloric acid slowly and with vigorous stirring until precipitation of $Co(NH_3)_6Cl_3$ is complete. About 400 ml are required.

9. Filter off the salt and wash with several portions of a solution which is 50% in ethanol and 50% concentrated hydrochloric acid.

Evaluation of the Product

Cobalt nitrate hexahydrate containing 0.15% nickel, which corre-

sponds to 0.75% on the basis of cobalt, was subjected to the purification procedure I. Two batches of $Co(NH_3)_6Cl_3$ were prepared. The hexammine salt was heated in a vicor vessel with sulfuric acid to completely decompose the complex. The cobalt sulfate was dissolved in some water and analyzed according to the analytical procedure described in Chapter V. Results of several of these analyses are presented in Table 8.

Inspection of the table clearly indicates that the method is quite effective in reducing the nickel content from 0.75% to as low as 0.00076%. When developing the analytical procedure of Chapter V, the salts were used as obtained in step 9 of the purification procedure I. However it is probable that even better material can be obtained by further recrystallizing the hexammine salts (i.e., repeating steps 8 and 9 of the purification procedure I).

Preparation of "Nickel-Free" Cobalt(II) Sulfate

For preparation of "nickel-free" cobalt, samples of cobalt were treated in a manner parallel to the analytical procedure described in Chapter V.

Purification Procedure II

1. Prepare, according to steps 1 through 7 of the procedure outlined in Chapter V, a sample of cobalt(III) pentammine complex containing about one gram of cobalt in a total volume of between 50 and 100 ml.

2. Add approximately 2 ml of 0.01 F PAN, shake 10 seconds, and allow to stand for at least 3.5 minutes.

3. Extract the solution from step 2 with three 8-ml portions of chloroform and discard the chloroform extract.

Table 8. Representative Results for Evaluation of Nickel in Cobalt Salts Prepared via $Co(NH_3)_6Cl_3$. (The Starting Material contained 0.75% Nickel based on Cobalt.)

Batch Number	Mg Cobalt Analyzed	µg Nickel Found	% Ni Based on Cobalt
1	470	3.6	0.00077%
1	705	5.5	0.00078%
1	940	7.0	0.00074%
2	64.5	3.4	0.0055%
2	96.8	5.0	0.0050%
2	120	6.3	0.0055%

4. Repeat steps 2 and 3.

5. Evaporate, on a hot plate, the solution of cobalt(III) pentammine from step 4. As the solution is concentrated by evaporation, ammonium salts are the first to settle out. Continue the evaporation until some red needles of the cobalt(III) pentammine salt begin to form on the surface of the ammonium salt already settled out.

6. Decant, while still hot, the red liquor containing the cobalt (III) pentammine complex into a vicor vessel.

7. Heat the red liquor in the vicor vessel until a thick slurry results.

8. Add about 2 ml of concentrated sulfuric acid and evaporate to dryness.

Discussion

Samples of cobalt prepared according to the above procedure were tested for nickel content by the procedure outlined in Chapter V, and no nickel could be detected. It should be pointed out that although the procedure is designed for purification of one gram of cobalt, considerably larger amounts can be handled. In the procedure discussed in Chapter V it was found that a maximum of about one gram of cobalt could be completely masked against reaction with PAN. When greater amounts of cobalt are present, some cobalt panate is formed and is coextracted with the nickel panate. Although the formation of even small amounts of cobalt panate must be prevented in the analytical procedure for nickel, it is inconsequential in the purification process here described. Also once "nickel-free" cobalt(III) pentammine has been obtained at step 4 of the procedure here described, very large amounts of the cobalt com-

pound can be handled throughout the remaining steps.

It should also be pointed out that cobalt(III) hexammine salts can be substituted for cobalt(III) pentammine salts. If these salts are readily available, it is advantageous to use them as starting material. If such is the case, step 1 of the purification procedure II outlined here would, of course, be omitted.

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VITA

Joe Allen Mann was born June 20, 1941, in Ronceverte, West Virginia, to Allen Ludington Mann and Margie Morgan Mann. He attended Greenbrier High School in Ronceverte and was graduated, valedictorian, in June 1959. In September, 1959, he entered West Virginia University, Morgantown, West Virginia, and was graduated with a B.S. degree in Chemistry in June of 1963.

In August, 1963, he was married to Mary Elizabeth Moran of White Sulphur Springs, West Virginia.

In September, 1963, he was appointed a Graduate Teaching Assistant in the School of Chemistry at the Georgia Institute of Technology, Atlanta, Georgia. In September, 1966, he was appointed Instructor in the School of Chemistry at Georgia Tech and served in that capacity until December, 1968.